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SOLUTION CYCLES AS APPLIED TO STEP-UP TRANSFORMERS FOR TEMPERATURES.*

BY

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In 1755 Dr. William Cullen produced ice by a vacuum machine. Water at ordinary temperature was placed in an air-tight vessel, the air removed and the pressure reduced by a vacuum pump until the water boiled. The heat necessary for evaporation was absorbed from the water itself and the operation continued until the residual liquid water became so cool that it froze.

Over half a century later in 1810 Sir John Leslie combined Cullen's air pump with a vessel of strong sulfuric acid for absorbing the water vapor, and is reported to have produced from one to one and a half pounds of ice in a single operation. This was probably the first practical application of the fact that a solution will absorb vapor from pure liquid which is at a lower temperature than the solution.

Twelve years later Faraday [3] reported the results of quantitative investigations of the increase in temperature of a boiling solution above that of the boiling pure solvent. The greatest elevation in boiling observed was about 106° F. for a potassium salt.

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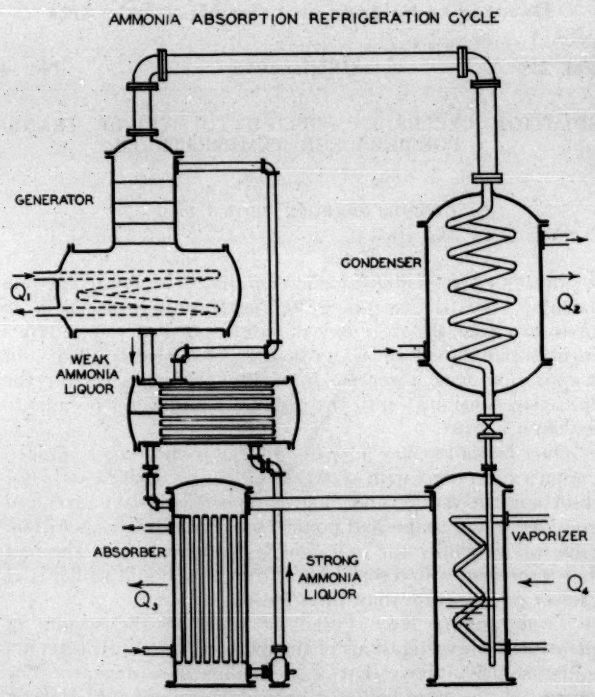
These properties of solutions were used by Carré and later (1867) by R. Reece in the development of the first solution cycle, the ammonia absorption cycle for refrigeration. Figure 1 shows the essential features of this cycle in its modern form, which is in wide-spread use today.

FIG. 1.



The ammonia absorption refrigeration cycle.

An example of the simple elemental solution vapor compressor incorporated in a refrigeration cycle. Low pressure ammonia vapor is supplied from the vaporizer in the lower right-hand corner to the absorber, and high pressure ammonia vapor is supplied from the top of the generator to the condenser. The solution vapor compressor is operated by heat, Q_1, supplied to the generator with the rejection of heat, Q_3, from the absorber. The condenser and vaporizer represent the refrigeration process which absorbs heat, Q_4, at low temperature in the vaporizer and rejects the heat, Q_2, at a higher temperature from the condenser. The two processes together make a refrigerating cycle.

The full significance of Faraday's report on the increase in boiling point of solutions was first appreciated by Spence who reported to the British Association at Exeter in 1869 that the exhaust steam from a steam engine when liberated at atmospheric pressure (temperature 212° F.) and absorbed in a saline solution having a boiling temperature higher than that of water, would raise the temperature of this saline solution to its own boiling point. This fact is of major importance in the development of solution cycles and is apparently not generally appreciated today.

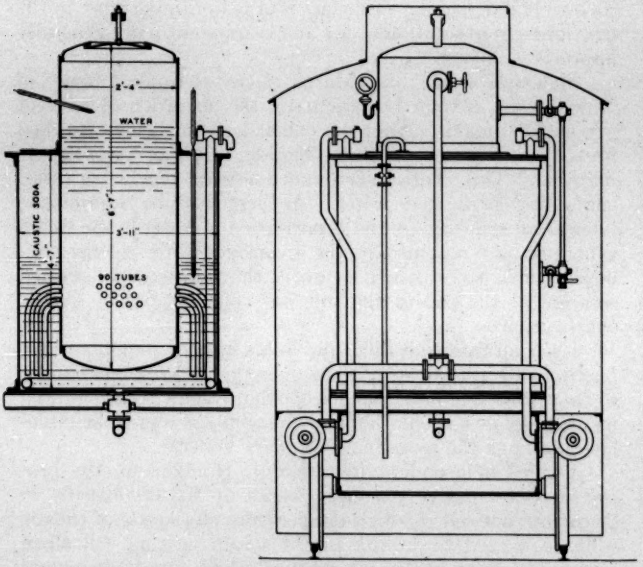
About the same time (March 12, 1872) Emile Lamm [7] of New Orleans obtained a patent for the operation of a street car with a steam engine; the exhaust steam being absorbed into a solution of calcium chloride or other appropriate material. This solution surrounded a steam generating vessel containing preheated water. As described by Lamm the latent heat removed by the vaporization of water in the steam generator was returned to the steam generator by the condensation of the exhaust steam in the solution; the diluted solution at the end of the run was concentrated by simple evaporation.

A second Spence,[17] following in his father's footsteps, proposed, in 1874, to operate a steam engine in a manner similar to that proposed by Lamm, except that caustic soda was used instead of calcium chloride and the solution was to be circulated through the pipes in an ordinary boiler.

A third independent investigator, Honigmann, the proprietor of extensive chemical works at Aix-la-Chapelle in Germany, noticed the high temperature of a kettle of caustic solution caused by a leak in the steam heating coil when inspecting operations in his chemical plant, and built several fireless locomotives on the same principle early in the next decade. Figure 2 illustrates one of the units of this type described by Riedler [18] who made extensive tests of the Honigmann fireless locomotive in 1883. Figure 3 is a log of Riedler's experiment 22 in which the engine drew a car with a load of 19 tons up and down the track for one hour, and then two empty cars of total weight 14.5 tons for the remainder of the run, which lasted for almost four hours on a single filling of caustic of 1,620 lbs. containing 15.7 per cent. water.

At the end of this time the caustic solution amounted to 2,450 lbs. containing 43.8 per cent. water. During the first hour and 20 minutes, up to the point *A*, steam was used in braking the locomotive at the end of the run; from that point on only the hand brake was used. At the end of 2 hours and

FIG. 2.



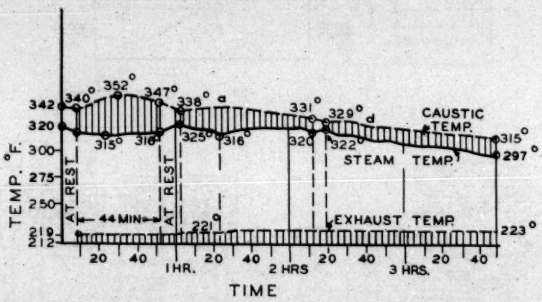
Honigmann's fireless locomotive tested by Professor Riedler.

40 minutes, at the point *D* on Fig. 3, the water in the boiler had been reduced to only 3.14 inches above the tubes while the caustic level was 14.6 inches above this.

Following this successful experiment numerous commercial installations were made and there was great interest in the technical press until about 1888 when interest seems to have suddenly subsided.

In all of these operations the reconcentration of the dilute solution was accomplished by simple evaporation. It was quite generally recognized that the thermal efficiency of this process was relatively low, as more coal was consumed in evaporating, or "boiling down" of the solution than is required for evaporation of the same quantity of water under ordinary circumstances. In order to improve the efficiency of the operation Honigmann obtained patents proposing to add a firebox to his "fireless" locomotive and concentrate the solution in a direct fired vessel under the same pressure as employed in the cylinders in the engine,[4] and to use a double effect evaporator for concentrating the spent solution.[4a]

FIG. 3.

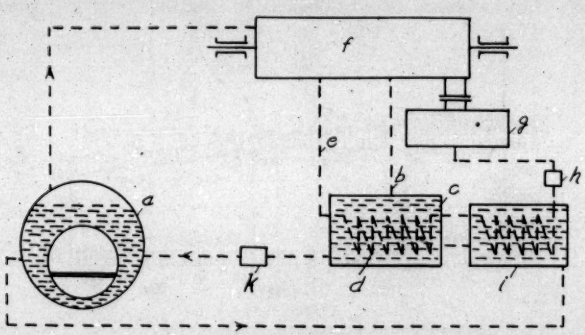


Log of Riedler's experiment 22 with Honigmann's fireless locomotive as shown in Fig. 2.
The temperature is plotted as a function of time giving the temperature of the caustic solution, the temperature of the steam generated in the boiler, and the temperature of the exhaust steam from the engine as supplied to the caustic solution.

Due, probably, to the low efficiency of these operations the promising start made by Honigmann was apparently abandoned by 1888 and nothing more is heard of such solution cycles until 1908 when Schneevogl [14] obtained a French patent covering the use of a counter-current heat exchanger between the high temperature concentrated solution flowing from the concentrator to the absorber, and the dilute solution flowing from the absorber to the concentrator. This is an important development from the standpoint of efficiency in such cycles, and is shown in Figs. 1, 6, 7, 10.

An important feature of the use of solutions for the generation of power is the possibility of storing concentrated solution and water without loss in available energy, and generating steam by dilution of the concentrated solution according to the method already discussed. In 1911 this feature was covered by U. S. patent granted to D'Equevilley-Montjustin [2] who utilized the storage principle for the purpose of operating submarines when submerged by means of a steam engine whose exhaust was absorbed into the solution. The solution was concentrated in an evaporator by steam from the direct-fired boiler when running on the surface.

FIG. 4.



Power solution cycle of Pape.

A is the solution boiler supplying steam to the turbine *F*. An equal quantity of steam is bled from turbine *F* through line *B* and absorbed in absorber *C* where the heat of absorption is used to vaporize water in coil *G*. The steam so formed is fed to turbine *F* through line *E*, condensed in *G* and forced by pump *H* through the coil in *I* to the vaporizing coil *D* in absorber *C*. The dilute solution formed in absorber *C* is forced by pump *K* into the solution boiler *A*, and the concentrated solution transferred from *A* to heat exchanger *I* where it is cooled giving up its sensible heat to the cold condensate from the engine. The cooled solution is then passed through absorber *C* where it absorbs the steam bled from turbine *F* through line *B*.

Interest in the use of solutions for the generation of power and for stepping up the temperature in heat cycles began to increase in 1920, particularly in Europe. In that year Pape [11] obtained a German patent covering the cycle shown in Fig. 4. The following year Koenemann [6] obtained his first German patent which was followed by others in Austria, Great Britain and in the United States.

Figure 5 shows the early form of the Koenemann transformer, in which concentrated solution was withdrawn from the lower part of vessel 3 at point 4 and passed into the lower part of vessel 7 through valve 6. Low pressure vapor enters

FIG. 5.

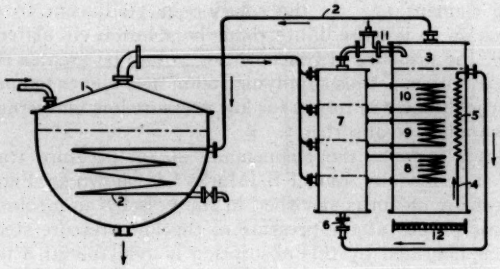


FIG. B

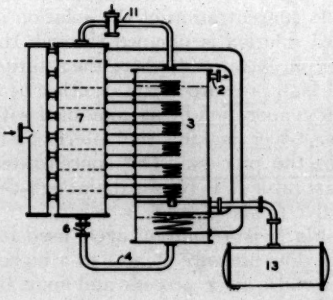
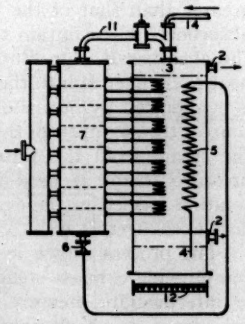


FIG. C



Early form of Koenemann steam pressure transformer as disclosed in British Patent Number 178,829 of January 4, 1923.

from kettle 1 into absorber 7 with dilution of the solution rising therein, the heat effect accompanying the absorption is supplied to concentrator 3 by flowing the diluted solution

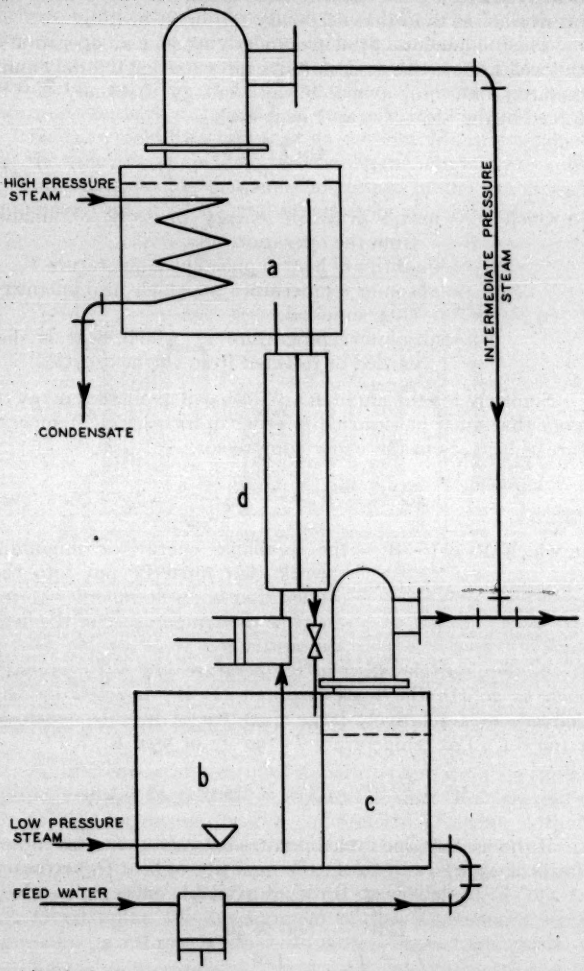
through the heat exchanger coils 8, 9 and 10, the dilute solution so formed flows out of the top of absorber 7 through valve 11 into concentrator 3 wherein the dilute solution becomes progressively more concentrated due to evaporation caused by the hot solution circulated from 7 through coils 8, 9 and 10, the final concentration being accomplished by the heating element 12. As the solution in 3 adjacent to any coil such as 10 is more dilute than the solution circulated in the coil, the pressure in concentrator 3 may be greater than that in absorber 7, thus supplying steam at a higher temperature through line 2 in return for low pressure low temperature steam supplied to absorber 7.

A later form of the Koenemann steam pressure transformer described by Lionel S. Marks [8] is shown in Fig. 6. Low pressure steam is absorbed in the vessel *B* in a solution of caustic potash at the pressure of the low pressure steam. The heat liberated by this absorption is available at a temperature approximating the boiling point of the solution and is used to boil water in the vessel *C*. The temperature of the water in vessel *C* approaches that of the solution in *B* and the pressure of the steam evolved from the water boiler *C* is greater than that of the low pressure steam supplied to the absorber. To maintain the concentration of the solution in the absorber *B*, the diluted solution is pumped through the heat exchanger *D* into the concentrator *A* where the solution is evaporated by means of high pressure steam or other heat source, the steam from this evaporation being combined with the steam from the water boiler making the intermediate pressure steam as used in the process. The concentrated solution formed in the evaporator *A* is returned through the heat exchanger *D* and a valve to absorber *B*.

The process shown in Fig. 6 is a solution cycle used for compressing exhaust steam (low pressure steam) to a higher or intermediate pressure for use in a process and may be considered as an alternate method to the mechanical compression of low pressure vapor.

The earliest suggestion of this kind was probably that of Lord Kelvin who proposed in 1852 the use of a compressor (a reversed heat engine) as a means for warming air. He showed that for a small temperature rise the quantity of

FIG. 6.



A later form of Koenemann's steam pressure transformer as described by Professor Marks.

heat required by an efficient heat engine to drive the compressor is less than that necessary for direct heating.

The fundamental principle underlying such an operation is the well-known thermodynamic expression for the maximum quantity of useful available work energy that may be obtained in the ideal (Carnot) heat cycle.

$$W = \frac{Q_1(T_1 - T_2)}{T_1}, \qquad (1)$$

in which W = useful available energy or work obtainable from the operation,
Q_1 = quantity of heat supplied at temperature T_1,
T_1 = absolute temperature at which heat quantity Q_1 is supplied,
T_2 = absolute temperature at which heat is discarded or rejected from the heat cycle.

Similarly for the minimum quantity of available energy or work that must be supplied in order to increase the temperature of heat, as in the vapor compressor,

$$\Delta G = -W = \frac{Q_1(T_2 - T_1)}{T_1}, \qquad (1a)$$

in which ΔG or $-W$ = the available energy or minimum work that must be put into the operation or cycle in order to increase the temperature of the heat quantity Q_1.

If the required elevation in temperature $(T_2 - T_1)$ is small such as 20° F. the work required $(-W)$ is small for the delivery of a relatively large quantity of heat Q_2 (such as 1,100 B.t.u.) at temperature T_2 (90° F. or 550° R.),

$$-W = \frac{Q_2}{T_2}(T_2 - T_1) = 2(20) = 40 \text{ B.t.u.}$$

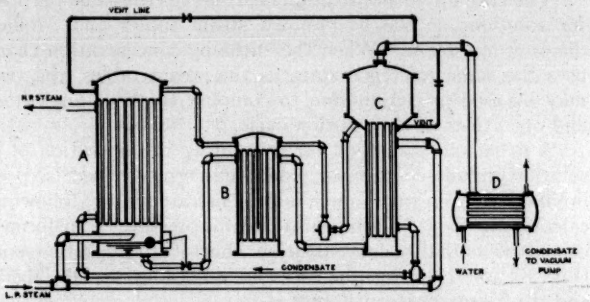
If the heat engine cycle operates between the temperature limits of 230° F. and 90° F. the quantity of heat Q_1 necessary at 230° F. to deliver 40 B.t.u. of available energy or work is

$$Q_1 = \frac{T_1 W}{T_1 - T_2} = \frac{690 \times 40}{120} = 230 \text{ B.t.u.}$$

Therefore only 230 B.t.u. are required by an ideal cycle to deliver 1,100 B.t.u. under these conditions. Even with the low efficiency of 70 per cent. in each, the engine and the compressor, giving an overall efficiency of about 50 per cent., 500 B.t.u. supplied to the heat power cycle is more than adequate to deliver 1,100 B.t.u. under these conditions.

Since an overall efficiency of 50 per cent. is easily attained in the solution cycle such as the Koenemann vapor compressor, the possible economic advantage in the use of such equipment under such conditions may be appreciated.

FIG. 7.



Solution steam pressure transformer for separation.

Low pressure steam is supplied to the absorber through the line at the lower left corner of the figure, and is absorbed in absorber *A* by the concentrated solution flowing from the heat exchanger *B* into the top of absorber *A*. The heat of this absorption is used to vaporize water supplied to the space outside the tubes of the absorber *A* at a higher pressure than the low pressure steam. The high pressure steam so formed is withdrawn from the upper left-hand side of the absorber as indicated. The dilute solution formed in the absorber passes out the bottom of the absorber through a flow control valve into the heat exchanger *B* in counter-current heat exchange with the concentrated solution flowing to the absorber. The preheated dilute solution then enters the bottom of the concentrator or evaporator *C* where the steam absorbed in absorber *A* is again liberated at a lower pressure and condensed in condenser *D*. The concentrated solution so formed in evaporator *C* is picked up by the pump and forced through the counter-flow heat exchanger to the absorber. In the case considered by Mr. A. M. Selvey the heat of condensation of the steam from evaporator *C* was used to heat water in the condenser *D* for use in the laundry and club.

A different arrangement of apparatus but applying similar principles was suggested by Praetorius, and is of interest as it provides a means for the compression of vapor without requiring any other source of heat than the low pressure vapor itself. Figure 7 is a diagrammatic representation of such an arrangement as it might be constructed.

Overlapping the development of the Koenemann steam pressure transformer other advances have been made in

Europe, and in this country, notably by Wm. H. Sellew. A theoretical treatment of the method of computing the performance of such solution cycles, based on the thermodynamic properties of the solution used, was first presented by Frederick Merkel [9] of Dresden. Because of lack of data concerning the properties of caustic potash and soda, Merkel was obliged to make simplifying assumptions in the construction of his enthalpy-concentration chart.

Merkel's pioneer work in the development of these charts has been continued in Germany by Bošnjaković [1] and by W. L. McCabe [10] in this country.

The enthalpy-concentration chart serves the same purpose for solutions as the well-known steam tables and Mollier diagram for steam. When the enthalpy-concentration chart uses the same reference state as the steam tables, the two may be used in conjunction to compute the heat quantities and operations of the solution cycle.

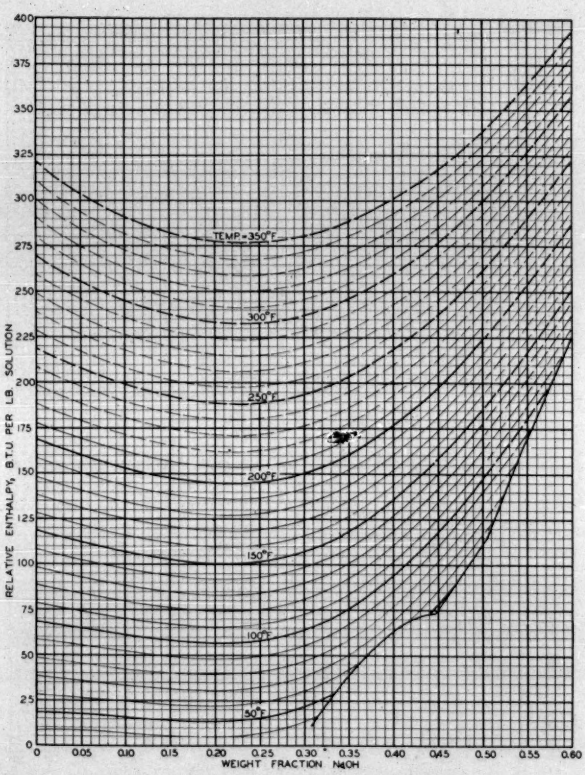
A satisfactory method for computing the operation of a solution thermo-compressor, which has been verified by preliminary tests on small units, is demonstrated in the following calculation for a Koenemann steam pressure transformer using the enthalpy-concentration chart [10] for caustic soda (Fig. 8) and Dühring plot (Fig. 9) according to McCabe,[10] and the Keenan [5] steam tables.

Using the arrangement shown in Fig. 7, with low pressure steam supplied at 20 lbs. per sq. in. abs. to deliver high pressure steam at 49 lbs. per sq. in. abs.,

Operating Conditions, Cycle, Fig. 7:

Condensing temperature of l.p. 20 lb. steam	= 228° F.
Temperature drop from steam to solution	= 30
Temperature of concentrated solution in concentrator	= 198° F.
Temperature of saturated h.p. steam (49 lbs.)	= 280° F.
Temperature drop absorber to boiling water	= 25
Temperature of solution in absorber	= 305
Allowed boiling temp. dilute solution 20 p.s.i. abs.	= 315
Concentration dilute solution in absorber (Fig. 9)	= 52.5%
Assume pressure in concentrator	= 1.0 p.s.i
Then concentrated solution in concentrator	= 60%
Temperature difference cold end (concentrator) of heat exchanger	= 30° F.
Temperature of 52.5% solution entering concentrator	= 228° F.

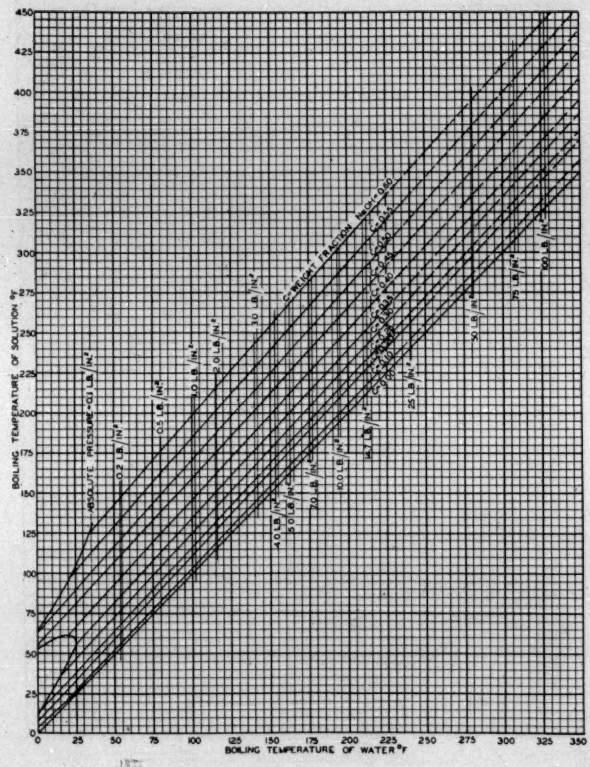
FIG. 8.



Enthalpy ("heat content") of a lb. of sodium hydroxide water solution as referred to pure liquid water at 32° F. plotted as a function of the concentration of the solution.

These heat quantities may be used directly in conjunction with the usual steam tables to determine the heat effects of evaporation, absorption, or changes in temperature of the solution within the cycle.

FIG. 9.



Duhring plot of caustic soda water solution.

The temperature at which the solution boils is plotted as a function of the temperature at which pure water boils when under the same pressure. This is a most convenient way of leveling and comparing the boiling points of solutions and solvents.

Specific Enthalpies (per lb.):

Steam at 20 p.s.i. ..... 1,156 B.t.u. (saturated)
Steam at 49 p.s.i. ..... 1,173.2 B.t.u. (saturated)
Steam at 1 p.s.i. ..... 1,148.9 B.t.u. @ 198° F.
60% solution @ 198° F. = 285 B.t.u.; @ 290° F. = 352
52.5% solution @ 228° F. = 258 B.t.u.; @ 315° F. = 316.8

HEAT BALANCES ON BASIS OF 1 LB. LOW PRESSURE STEAM INTO ABSORBER.

Heat Balance Around Absorber and Heat Exchanger

Quantity 52.5% solution leaving absorber $\frac{60}{60 - 52.5} = 8$ lb.

Quantity 60% solution entering absorber = 7 lb.

Heat In		*Heat Out*	
1# Steam 20 p.s.i.	= 1,156 B.t.u.	Delivered to boiler	= 1,087 B.t.u.
7# 60% sol. @ 198° F.	= 1,995	8# 52.5% sol. @ 228° F.	= 2,064
	3,151		3,151

$\frac{1,087}{11,73.2 - 67.9} = 0.98$ lb. h.p. steam per lb. l.p. steam to absorber.

Heat Balance Around Concentrator:

Heat In		*Heat Out*	
8# 52.5% sol. at 228° F.	= 2,064	7# 60% sol. @ 198° F.	= 1,995
By condensing 20 p.s.i. steam	= 1,079.9	1# Steam @ 198° F. 1 p.s.i.	= 1,148.9
	3,143.9		3,143.9

$\frac{1,079.9}{959.9} = 1.125$ lbs. sat. steam at 20 p.s.i. to concentrator

$\frac{1 + 1.125}{.98} = 2.167$ lbs. total low pressure steam (20 p.s.i.) to deliver 1 lb. h.p. steam (49 p.s.i.). Allowing 5% for radiation, about 2.275 lbs. of p.s.i. steam required for 1 lb. 49 p.s.i. steam, or an efficiency of conversion of 44%.

Heat Balance Around Heat Exchanger:

In		*Out*	
8# 52.5% solution @ 315° F.	= 2,534.4 B.t.u.	@ 228° F.	= 2,064 B.t.u.
7# 60% solution @ 198	= 1,995	@ 290° F.	= 2,465.4
	4,529.4		4,529.4

The practical application of such a solution cycle (Fig. 7) has been carefully studied by A. M. Selvey [16] of the Detroit Edison Co. who makes the following comments.

The Koenemann cycle has, however, two useful applications in the low-pressure low-temperature non-corrosive field. It can elevate low-pressure steam to a medium pressure by means of the addition of high-pressure steam, called combination, or it can elevate medium-pressure steam to a higher pressure.

This latter is called separation because the increased availability is obtained by rejecting a portion of the supply as exhaust steam.

Combination is an inexpensive method of increasing the availability of exhaust steam or increasing the steam pressure to permit the addition of several stages of evaporation to chemical manufacturing processes. The addition of one high-pressure boiler and the use of a Koenemann transformer may be a substitute for adding a number of low-pressure boilers.

Separation also has an interesting practical application in the production of relatively high-pressure steam when medium-pressure steam is the only available source of heat. This is obtained as in Fig. 7 by reversing the usual positions of the absorber and concentrator.

A comparison was made by the writer of the performance of a pressure transformer and an electrically-driven compressor for increasing district-heating steam pressure at 45 p.s.i. abs. to 95 p.s.i. for use in certain laundry equipment operating at a high temperature corresponding to the increased saturation pressure. The laundry considered in the writer's study was situated in an athletic-club building where it was not convenient to install a boiler plant with a twelve to fifteen story chimney, and where the only source of steam was the district-heating main in the street. The compressor was installed as the most satisfactory means of raising the steam pressure. The study which considered the hypothetical operation of a Koenemann transformer in place of the compressor, showed that the transformer was economical only when part or all of the rejected low-pressure exhaust steam could be used for heating water for the laundry and club use. Based upon curves indicating the probable hourly variation during the day of the use of steam and hot water, and assuming that all low-pressure exhaust steam could be utilized for water heating, the operation of the transformer showed a possible annual operating saving of 50.3 per cent. exclusive of capital charges.

The possibilities of the Koenemann steam-pressure transformer appear to warrant additional chemical and metallurgical research.

William H. Sellew was apparently the first, at least in this country, to appreciate the full significance of the Carnot principle as expressed in equation (1) as applied to solution cycles. The quantity of work, W, indicated by equation 1 is the maximum which may be obtained only under certain definite ideal conditions, 3 in number:

1. All of the heat that is received by the system that is converting heat into work must be received at T_1. No heat can be allowed to enter at any lower temperature.

2. All of the heat that leaves the system must leave at the temperature T_2. No heat must be allowed to leave at a higher temperature.

3. Every step or process in the operation or cycle must take place reversibly. This requirement is somewhat more difficult to visualize and much more difficult to approach in practice than the other two, as it rules out friction, throttling,

flashing, the addition of a cool fluid to a warmer one, temperature heads in heat transfer and all other operations that do not take place under equilibrium or reversible conditions. Although this requirement can be approached, it is impossible of complete realization in any practical operation.

These three requirements are necessary and sufficient for realization of the Carnot efficiency. It is not necessary to postulate any particular type of equipment, any particular kind of cycle, or any particular working substance. Within the system other forms of energy may be involved, such as electrical energy, or chemical energy, provided only that these three requirements are met.

In the Rankine (steam engine) cycle using superheated steam, the heat enters the cycle largely at the saturation temperature, or the temperature at which the water vaporizes. The heat in the superheat is a relatively small part of the total heat entering the cycle. In order to raise the saturation temperature, increased pressures as high as 2,000 to 3,200 lbs. per sq. in. are being used. By the proper use of aqueous solutions, all of the heat enters the cycle at the temperature of superheated steam, because the vapor formed by boiling a solution is, *per se*, "superheated," i.e. at a temperature above boiling water at the same pressure. Furthermore the solution may be so chosen as to have a high boiling point at moderate pressures, thereby gaining the efficiency of high pressure cycles or of combined mercury-steam cycles.

The use of solution cycles makes possible the fulfillment of the first two conditions for attaining the Carnot efficiency in a flexible and convenient manner. It remains, therefore, only to limit the irreversible processes within the cycle to attain an efficiency that will approach the Carnot efficiency as calculated from the two terminal temperatures. By heat exchange, bleeding of prime movers, and absorption of vapors, and other devices not possible to the one compound cycle, irreversible processes can be reduced to a minimum or as far as economically justified.

For heating and cooling operations heat Q_1 supplied at a high temperature T_1 to one process which rejects heat Q_2 at a lower temperature T_2 may be used for operating a second process which absorbs heat Q_4 at a low temperature T_4 and

rejects as heat Q_3 at a higher temperature T_3, the heat Q_4 plus the necessary available energy ΔG which in this case is supplied as W from the first process.

An energy balance around such an operation clearly indicates

$$Q_1 + Q_4 = Q_2 + Q_3. \tag{2}$$

If the operations are conducted in a reversible manner so that equation (1) may be applied,

$$Q_1\frac{T_1 - T_2}{T_1} = \frac{T_3 - T_4}{T_3}Q_3 = \frac{T_3 - T_4}{T_4}Q_4,$$

$$\frac{Q_3}{Q_1} = \frac{T_1 - T_2}{T_1} \times \frac{T_3}{T_3 - T_4}, \tag{3}$$

$$\frac{Q_4}{Q_1} = \frac{T_1 - T_2}{T_1} \times \frac{T_4}{T_3 - T_4}. \tag{4}$$

Equation (3) expresses the ideal (Carnot efficiency) coefficient of performance for a solution heating cycle when Q_2 is not available for heating.

$$\frac{Q_3}{Q_1} = \frac{\text{heat delivered for heating}}{\text{heat supplied for operation}}.$$

Equation (4) expresses the ideal coefficient of performance for a solution refrigerating cycle.

$$\frac{Q_4}{Q_1} = \frac{\text{heat absorbed for refrigeration}}{\text{heat supplied for operation}}.$$

If T_2 is the same as T_3 as is frequently the case, the heat quantity Q_2 is added to Q_3 for the heating operation, and the actual coefficient of performance (C.P.) becomes

$$\frac{Q_3 + Q_2}{Q_1} = \frac{Q_1 + Q_4}{Q_1} = 1 + \frac{Q_4}{Q_1} \tag{5}$$

or

$$\text{C.P.}_{\text{Heating}} = 1 + \text{C.P.}_{\text{Refrigeration}}. \tag{5a}$$

Since the quantity of cooling water required by an air conditioning or refrigerating cycle is frequently an important factor, the equivalent term total heat rejected $(Q_2 + Q_3)$ per unit of refrigeration is of interest,

$$\frac{Q_2 + Q_3}{Q_4} = \frac{Q_1 + Q_4}{Q_4} = \frac{Q_1}{Q_4} + \frac{Q_4}{Q_4} = \frac{1}{\text{C.P.}} + 1. \qquad (6)$$

Equation (6) gives the quantity of heat rejected from a solution refrigeration cycle for a unit of heat absorbed at the low temperature. This heat quantity is proportional to the quantity of cooling water required only if all heat is rejected isothermally at $T_2 = T_3$ as this was assumed in deriving the equation.

In the elemental refrigeration cycle shown in Fig. 1, under the same conditions ($T_2 = T_3$), the ideal coefficient of performance is

$$\frac{Q_4}{Q_1} = \frac{T_1 - T_2}{T_1} \times \frac{T_4}{T_2 - T_4}. \qquad (7)$$

If, as a very rough approximation, the solution is assumed to follow the Ramsay and Young Rule [12] for boiling temperatures of solution and solvent (water) when under the same pressure,

$$\frac{T_S}{T_W} = \frac{T_1}{T_2} = \frac{T_3}{T_4} = \frac{T_2}{T_4} = k \text{ (a constant)}, \qquad (8)$$

where T_S = absolute boiling point of solution,
T_W = absolute boiling point of pure volatile component at the same pressure.

Then by substitution from equation (8), equation (7) becomes

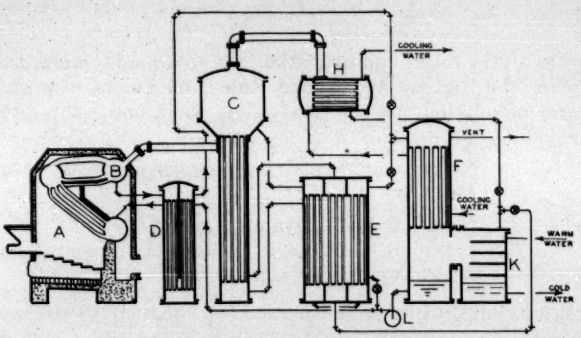
$$\frac{Q_4}{Q_1} = \frac{1}{k}. \qquad (9)$$

Although this expression is not rigorous for any known solution it helps to clarify the relationships between the coefficient of performance in elemental refrigeration cycles such as Fig. 1, and the properties of the solution used. In all such cases k, which corresponds to the slope of the line in Fig. 9, is greater than unity and the coefficient of performance for the simple refrigeration cycle of Fig. 1 using such a solution must be less than unity. If, however, a solution is employed for which T_S/T_W is less at low pressure than at high pressure a higher coefficient of performance can be obtained because T_1, the temperature of heat input, is thereby raised.

Equations (4) and (5) show that, for constant T_2, T_3 and T_4, high coefficients of performance are dependent upon high temperatures of heat supply (T_1). Therefore any convenient type of solution may be used to attain high efficiency provided the cycle is so constructed as to absorb heat at a high temperature (T_1) regardless of the vapor pressure characteristics of the solution used.

The possibility of high temperature heat input with all of the heat entering the cycle at the maximum temperature is a most important characteristic of solution cycles which has only recently been appreciated.

FIG. 10.



Direct-fired double-effect concentration solution cycle as applied to the refrigerating of water as required for air-conditioning units.

Warm water supplied to the vaporizer K is cooled by vaporization of part of the water and the refrigerated water so formed is removed as cold water. The low pressure water vapor formed in the vaporizer K is absorbed in absorber F by the concentrated solution entering the top of absorber F from the two counter-flow heat exchangers. The dilute solution so formed is collected at the bottom of the absorber, picked up by pump L and forced through the heat exchangers E and D outside the tube to the concentrators C and AB. The vapor formed from concentrating this solution in AB is used to boil solutions in concentrator C and the condensate so formed passed through the counter-flow heat exchanger E to the top of vaporizer K. The concentrated solution withdrawn from B passes through the heat exchanger D to the top of absorber F. The vapor formed in concentrator C is condensed in condenser H and brought to the top of the vaporizer K. The concentrated solution formed in concentrator C flows through the heat exchanger E and enters the top of absorber F. The heat of absorption of the low pressure vapor in absorber F is transferred to cooling water flowing outside the tubes in the absorber. This cooling water may then flow through condenser H in series with absorber F, or a fresh supply of cooling water may flow to condenser H as desired.

Sellew [15] obtains a high temperature of heat input and corresponding high efficiency by the use of multiple effect concentration and, when desired, multiple effect absorption. Figure 10 shows the flow diagram of such a unit used for

refrigerating water as is required for air conditioning units. The first concentrator, A, is shown as direct fired but could be a steam heated evaporator such as the second effect C if desired. The following calculations representing efficient conditions will explain the operation of such a cycle.

Operating Conditions, Cycle, Fig. 10:

Cold water to be cooled to 40° F. (corresponding pressure 0.1217 p.s.i.)
Cooling water available at 70° F. to condense vapors at 90° F. and 0.698 p.s.i.
Actual solution temperature in absorber F ..... 90° F.
Temperature difference to allow for departure from equilibrium .... 7° F.
Theoretical boiling temperature of solution in absorber F 97° F. at 0.1217 p.s.i.
Corresponding concentration of dilute solution from absorber F 45%
Concentrated solution from evaporator C. & B. 50%
Boiling temperature 50% solution under 0.698 p.s.i. in C ..... 162° F.
Allowed temperature drop over heating surface in C ..... 20° F.
Condensing temperature steam in evaporator C 182° F. at 7.849 p.s.i.
Boiling temperature 50% solution under 7.849 p.s.i. in A ..... 260° F.
Cold end temperature difference heat exchangers D and E ..... 15° F.
Temperature of 50% solution and condensate from D and E ..... 105° F.

Specific Enthalpies (per lb.):

Steam 7.849 p.s.i.	1,138 B.t.u. (saturated)	1,175 B.t.u. at 260° F.
Water condensate	73 B.t.u. at 105° F.	58 B.t.u. at 90° F.
Steam 0.698 p.s.i.	1,095 B.t.u. (saturated)	1,132 B.t.u. at 162° F.
Steam 0.1217 p.s.i.	1,077 B.t.u. (saturated)	

From chart (Fig. 8)
50% Solution at 105° F. 147 B.t.u.
45% Solution at 90° F. 107 B.t.u.

Flow Quantities:

For 1 lb. evaporation, 50% solution $= \frac{0.45}{.50 - .45} = 9$ lb.

45% solution $= \frac{.50}{.50 - .45} = 10$ lb.

FOR 1 LB. EVAPORATION IN C:
Heat Balance Around C and E:

Heat In		*Heat Out*	
10 lbs. 45% sol. at 90° F.		1 lb. steam 162° F.	
4 $= 10 \times 107$	= 1,070	0.698 p.s.i.	= 1,132 B.t.u.
By condensing steam	= 1,385	9 lb. 50% sol. at 105° F.	= 1,323 B.t.u.
	2,455		2,455

Lbs. steam from $A = \frac{1,385}{1,175 - 73} = 1.26$

50% solution from $A = 1.26 \times 9 = 11.34$; 45% solution to D $1.26 \times 10 = 12.6$

Heat Balance Around A and D:

Heat In		*Heat Out*	
12.6 lbs. 45% sol. at 90° F.	= 1,348 B.t.u.	1.26 steam at 260° F.	= 1,481 B.t.u.
Heat supplied as Q_1 at T_1	= 1,800	11.34 lbs. 50% sol. @ 105°	= 1,667
	3,148		3,148

Heat Balance Around Condenser H:

Heat In		*Heat Out*	
1 lb. vapor	= 1,132 B.t.u.	In cooling water Q_2	= 1,074 B.t.u.
		1 lb. condensate	= 58 B.t.u.
	1,132		1,132

Heat Balance Around Vaporizer K:

Heat In		*Heat Out*	
1 lb. condensate at 90° F.	= 58 B.t.u.	2.26 lb. vapor @ 40° F. = 2.26 × 1,077	= 2,434 B.t.u.
1.26 lb. condensate at 105° F.	= 92 B.t.u.		
Heat absorbed Q_4 at T_4	= 2,284		
	2,434		2,434

Heat Balance Around Absorber F:

Heat In		*Heat Out*	
20.34 lb. 50% solution at 105° F.	= 2,990 B.t.u.	22.6 lb. 45% solution @ 90° F.	= 2,418 B.t.u.
2.26 lb. vapor at 40° F.	= 2,434	In cooling water Q_3	= 3,006
	5,424		5,424

Overall Heat Balance for 1 lb. water evaporated in C:

Heat In	*Heat Out*
Q_1 = 1,800 B.t.u.	Q_2 = 1,074 B.t.u.
Q_4 = 2,284	Q_3 = 3,006
4,084	4,080

Performance:

$$\text{C.P.} = \frac{Q_4}{Q_1} = \frac{2,284}{1,800} = 1.27$$

The importance of the second effect concentrator may be seen by comparing the first two cases given in Table I which summarizes the results of other similar calculations. The addition of the second concentrator as shown in Fig. 10 enables the same quantity of heat to concentrate an additional quantity of solution, thereby increasing the coefficient of performance. This is made possible by the greater availability of the heat used at the higher temperatures (260° F. instead of 162° F.).

TABLE I.

Comparison of Solution Cycles for Cooling or Refrigeration of Water.

	Temperature °F. at					C.P.
	AB.	*C.*	*F.*	*H.*	*K.*	
Single Effect	—	162	90	90	40	0.735
Double Effect	260	162	90	90	40	1.27
Double Effect	363	226	105	130	40	1.135

The letters refer to pieces of equipment as identified in Fig. 10.

Although caustic soda solutions have been used in these calculations, other solutions are considered far more satisfactory. Caustic soda causes embrittlement of steel and its use therefore requires nickel or alloys in the fabrication of equipment. Its high viscosity is a serious disadvantage in the heat-transfer and fluid-flow phases of design. Other solutions having the desirable properties of caustic and relatively free from these disadvantages are known, but their thermal properties have not been determined with the completeness or precision with which the thermal properties of caustic soda solutions are known. However the performance of a solution cycle can be estimated within reasonably close limits without the complete and exact knowledge of the heat quantities as given by the enthalpy-concentration chart, Fig. 8.

The heat input to the cycle depends almost entirely upon the heat required (increase in enthalpy) to vaporize the water from the solution in the first concentrator. This heat quantity is related to the vapor pressure data of the solution through the fundamental thermodynamic equation

$$\frac{dp}{dT} = \frac{\Delta H}{T(V_v - \bar{V}_1)}, \qquad (10)$$

in which $\frac{dp}{dT}$ = the slope of the vapor pressure temperature curve,

T = the absolute temperature of the solution,

ΔH = the increase in enthalpy or heat required to vaporize unit weight of solvent from the solution,

V_v = the volume of unit weight of solvent vapor,

$\bar{V}_1$ = the partial volume (effective volume) of unit weight of liquid solvent in the solution.

Under ordinary pressure ranges, $\bar{V}_1$ is so small compared with V_v that $\bar{V}_1$ may be neglected without appreciable error.

By writing this equation, 10, for the solution, and also for the pure solvent (usually water) and dividing the latter by the former, the following equation is obtained:

$$\frac{dT_S}{dT_W} = \frac{\Delta H_W T_S V_S}{\Delta H_S T_W V_W}, \qquad (11)$$

in which $\frac{dT_S}{dT_W}$ = the slope of the line on the Duhring plot (Fig. 9),

ΔH_W = latent heat of vaporization of solvent from pure liquid solvent to saturated solvent vapor,

ΔH_S = latent heat of vaporization of solvent from solution to superheated solvent vapor at the same pressure,

T_W = the boiling point of pure solvent,

T_S = the boiling point of solution under the same pressure,

V_W = the specific volume of saturated solvent vapor, in equilibrium with pure liquid solvent,

V_S = the specific volume of superheated solvent vapor, in equilibrium with solution at the same pressure.

This equation is most useful when written for two different solutions which are compared at the same temperature and pressure, under which conditions the values for ΔH_W, T_W, and V_W are of course the same, and likewise T_S and V_S are the same. Under these conditions

$$\frac{dT_S}{dT_W} = \frac{\Delta H_W T_S V_S}{T_W V_W} \times \frac{1}{\Delta H_S},$$

in which $\frac{\Delta H_W T_S V_S}{T_W V_W}$ is a constant of the same value for the two solutions.

Therefore the heat required to vaporize the unit weight of solvent vapor from the solution varies inversely as the slope of the Duhring line. By plotting the vapor pressure data of another solution as has been done for caustic soda in Fig. 9, and determining the slope of the line for the two solutions at the same points on the diagram, the latent heat of vaporization of solvent from one solution may be determined from that of the known solution. That solution having the greater slope on the Duhring plot requires less heat for concentration, and similarly gives off less heat on absorption of the low pressure vapor.

When it is considered that many of the thermal quantities within the cycle tend to cancel each other, the external heat balance is not sensitive to small changes in the heat quantities within the cycle. The effect of relatively large differences in specific heat, for example, would be practically eliminated by the heat exchangers used in the cycle. It is therefore possible to determine, on the basis of the vapor pressure data of a solution, the significant heat quantities for determining the ideal thermodynamic efficiency; and by comparison with a similar cycle as computed for sodium hydroxide solutions, to estimate its actual coefficient of performance within reasonably close limits. The available data on a number of promising solutions indicate a slope for the Duhring line not less than that shown for the caustic soda solutions in Fig. 9, and the comparisons herein set forth on the basis of sodium hydroxide solutions are therefore also representative of results to be obtained by the use of other solutes.

Table II compares the energy costs for operation of electrical compressor refrigerators, solution, and steam-jet thermo-compressors of the same duty. Although the coefficient of performance of the electrically driven unit is much higher, the use of low cost heat energy enables the solution thermo-compressor to show more economical operation under present conditions. The C.P. of 1.2 used in Table II makes a small allowance from the computed value of 1.27 (Table I) for energy required for pumping solution.

The relatively high charges for energy and cooling water requirements in the case of the steam-jet are partially compensated by the simplicity of equipment, but the much lower

TABLE II.

Relative Operating Costs for Refrigerating Water to 40° F. with heat Rejected from the Cycle at 90° F.

	Coefficient of Performance.	Relative Quantity Energy Required.	Relative Costs for Energy.			Relative Quantity Cooling Water Required.
			Coal @ $5/ton Electricity $0.0125 KW.Hr.	$4.40/ton $0.0125 KW.Hr.	$14.15/ton $0.010 KW.Hr.	
Electrical Compressor	4.7	1.00	1.00	1.00	1.00	1.00
Double Effect Solution Compressor	1.2	3.92	0.284	.25	1.00	1.51*
Steam Jet Compressor	0.3	15.7	1.136	1.00	4.00	3.61

Coal assumed to have heating value of 13,500 B.t.u. and used with furnace efficiency of 70 per cent.

* This is a maximum value assuming isothermal rejection of heat. Actually the solution cycle rejects heat over a temperature range and the cooling water is heated to a higher temperature so that this figure in practice may be easily reduced to about 0.85.

operating costs of the double effect solution cycle appear favorable.

Under some conditions the quantity of cooling water required is a serious consideration in operating costs. If the cooling water is passed through the absorber and then the condenser as shown in Fig. 10, and more concentrated solutions used (such as 55 per cent. and 60 per cent.), the cooling water may be heated to a higher temperature and its quantity greatly reduced with only a small loss in the coefficient of performance (as indicated by the third line in Table I). As the concentration of the solutions is easily changed by modifying operating conditions, the solution thermo-compressor is flexible both as to changes in capacity with constant cooling water and to changes in cooling water at constant capacity by increased evaporation in the concentrator.

The low maximum pressure required for efficient operation of solution refrigerating cycles, less than atmospheric for the first two cases and only 2 atmospheres for case three of Table I, is an important advantage for many uses.

The capacity of a given steam-jet compressor, that is, the pounds of water vapor drawn in and compressed at fixed pressure, is approximately constant regardless of the amount of steam being used. Therefore flexibility in capacity is obtained by using a number of jets in parallel with manual or automatic control. If cooling water temperature rises the jet will fail, or strike back, until the suction pressure is correspondingly raised by increase in temperature of refrigerated water, unless the pressure of steam supply is increased. Steam-jet installations should have reserve steam pressure for increased cooling water temperature and consist of multiple jets in parallel for variation in capacity.

The solution compressor is readily adjusted to decreased loads, and increased steam pressure or temperature in the concentrator is all that is necessary to compensate for increased temperature of cooling water (case 3 Table I).

Mechanical compressors may be adjusted for decreased load but will not refrigerate the water to the desired temperature if the temperature of the cooling water rises beyond that for which the unit is designed.

In general there appear to be three fields in which the use of solution cycles may prove desirable. The most promising at present is probably for refrigeration, as for air conditioning and possibly the reversal of this operation for the purpose of heating buildings.

As a steam pressure transformer, the use of solutions appears promising in many cases. It is possible that future developments may indicate the use of such cycles for the generation of power. Simple cycles as were used by Honigmann are not economical and intensive development will be required before solutions may be employed advantageously in competition with the common means of generating power.

In the case of air conditioning, heating, and for the compression of vapors, advantages of low operating cost are indicated for the use of the solution cycle. Further engineering development and the use of non-corrosive solutions, now being studied, will reduce the original cost of solution cycle equipment so that the total savings in operation may be large, particularly in installations of moderate to large capacity.

The peculiar advantage in the storage of available energy

in the form of concentrated solution and pure solvent may hasten the application of the use of solutions in the generation of power where wide fluctuations in load may be expected.

The theoretical basis for the computation of such cycles is now well established, equipment can now be designed and performance computed. It is expected that engineering development will soon follow, making possible the practical application of the use of such solution cycles with the corresponding gain in operating economy.

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BEHAVIOR OF DIELECTRICS UNDER ALTERNATING STRESS.*

BY

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ABSTRACT.

The presence of maxima in the power factor-frequency and power factor-temperature curves of dielectrics has been explained by the Maxwell inhomogeneity theory and the Debye theory of polar molecular orientation. In order to ascertain the true cause of these maxima, a study has been made of the power factor of an essentially non-polar material with and without polar materials in dilute solution over extended ranges of frequency, 65 to 7.2 × 10^6 c.p.s., and temperature, 2.9° C. to 90° C.

The non-polar solvent is a mixture of paraffins having a pour point at 55° C. Small power factor maxima, 0.0003 in value, shifting over the audio frequency range with temperature variation, are observed for this solvent alone. Adding 3 per cent. phenol gives rise to molecular orientation maxima restricted largely to frequencies above 10^7 c.p.s. At the lower temperatures, these maxima are greatly broadened, so that there is apparently a small contribution at power frequencies. Adding 10 per cent. stearic acid gives similar results. The failure of these maxima to shift to lower frequencies at the lower temperatures is due to the failure of the inner viscosity to increase very much in the solid state. The variation of the inner viscosity is calculated from the reciprocals of the short time conductivities since the degree of ionic dissociation is found to be essentially independent of temperature. The viscosity may be regarded as a function of particle size and varies within the medium. Where power factor maxima shift with essentially undiminished magnitude over a wide frequency range at ordinary temperatures, such as those observed here in the solvent above, it is believed that the cause is the orientation of associated or polymerized polar aggregates of such size as to be affected by the larger viscosity changes approaching the macroscopic.

In the solid and amorphous states, the limited motion of ions leads to an ionic polarization as indicated by absorption curves of relatively large time constants and by high power factors in the low frequency range. The addition of organic acids greatly increases these effects and also increases the final conductivity. The true short time conductivity is largely caused by almost completely dissociated inorganic material.

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I. INTRODUCTION.

The subject of the loss in dielectrics under alternating stress has incited an enormous amount of both theoretical and experimental work ever since the observation of the pronounced heating in condensers by Siemens in 1864. The reasons for this are several: (1) the complexity of the behavior of the loss and the difficulty of separating the effects of the large number of contributing causes now known to exist; (2) the importance of the loss in its relation to the heating in electrical insulation with its consequent effect on the insulation breakdown strength; (3) the importance of the study of the loss in yielding information concerning the structure of matter.

The sources of dielectric loss under alternating stress may be divided into two general classes: (1) conduction; (2) dielectric absorption. The conduction, or irreversible charge flow, in dielectrics is highly anomalous and may be caused by a number of different types of ions. The last traces of conduction in pure hydrocarbons are evidently due to radioactive ionization as shown by Jaffé.[1] In commercial insulation, however, most of the ions arise from the dissociation of ionizable material, i.e., acids, etc. It was first found by Tank,[2] and later by Whitehead [3, 4, 5] and his associates, that the conduction in liquid dielectrics following the sudden application of a direct voltage is constant up to times of the order of 1 second, after which it falls gradually to a low final value. The initial conduction accounts for practically all of the a.c. loss in liquids and the loss is independent of the frequency. The conductivity (conduction for a unit cube per volt) depends on the concentration and mobility of the ions and decreases rapidly with decreasing temperature. There is no measurable effect of conductivity on the dielectric constant for the low values of ion concentrations present in insulators.

Dielectric absorption, or reversible charge flow as a decaying function of time following the sudden application of a constant stress, is the principal source of a.c. loss in solid dielectrics. It also contributes to the dielectric constant in the appropriate frequency range. This property of dielectrics is even more complicated than the conduction and a number of theories have been proposed for its explanation. In all

the simple theories, the absorption current is governed by a first order differential equation and so, all lead to the same form for the decaying function of time, namely, the negative exponential:

$$i_r(t) = EC_0\beta e^{-t/\tau}, \tag{1}$$

where C_0 is the geometric capacity, and τ is the time constant.

Regardless of the nature of the absorption, the dielectric properties for alternating fields may be calculated from the absorption curve by means of the superposition theorem as shown by von Schweidler,[6] and extended and applied by Whitehead and Baños.[7] This is perfectly general; the absorption curve is merely used as the response of dielectric to the unit e.m.f., and the a.c. properties follow mathematically. For the negative exponential absorption curve (1) written for unit capacity per volt, the expressions for the loss angle, δ, and dielectric constant, ϵ, as functions of frequency, $f = \omega/2\pi$, are

$$\delta = h\omega\tau/(1 + \omega^2\tau^2), \tag{2}$$

$$\epsilon = \epsilon_0[1 + h/(1 + \omega^2\tau^2)], \tag{3}$$

where h is the absorption constant equal to $\beta\tau$, the area under the absorption curve, and ϵ_0 is the dielectric constant at infinite frequency. It is assumed here and throughout this paper that h is small, as is usually the case for dielectrics. The loss angle, δ, may then be taken as equal to the power factor, sin δ. The power factor *vs.* log frequency curve goes through a symmetrical maximum of value, $h/2$ at a frequency, $f_m = 1/2\pi\tau$. Correspondingly, the dielectric constant decreases from $\epsilon_0(1 + h)$ to ϵ_0 as the frequency increases, the point of inflexion being f_m. Many experimentally obtained curves show this general behavior, for example, those obtained by Wagner [8] for a number of waxes, and by Race [9] for cable compounds.

The theories for the explanation of dielectric absorption and the associated a.c. behavior may be divided into two classes: (1) those dependent on conduction or ionic polarization, chief of which is the inhomogeneity theory of Maxwell, extended by Wagner; (2) those dependent on molecular phenomena only, as represented by the Debye theory of polar

molecular orientation. The inhomogeneity theory as developed by Wagner [8] gives

$$h_W = 9p(\lambda_1\epsilon_2 - \lambda_2\epsilon_1)^2/[\epsilon_1(2\epsilon_1 + \epsilon_2)(2\lambda_1 + \lambda_2)^2], \quad (4)$$

$$\tau_W = 8.85 \times 10^{-14}(2\epsilon_1 + \epsilon_2)/(2\lambda_1 + \lambda_2), \quad (5)$$

where material of properties, ϵ_2, λ_2, is distributed in concentration, p, in a medium of properties, ϵ_1, λ_1. The conductivity, λ, decreases as the temperature is lowered. This does not change h essentially, but it increases τ, so that lowering the temperature shifts the power factor maximum to lower frequencies, as observed. It is necessary, however, to have a conductivity, $\lambda > 10^{-11}$ mho cm.$^{-1}$ for $f_m > 10$ c.p.s., so that for dielectrics, the contributions from this mechanism can occur only in the low frequency range.

By assigning values of permanent electric moment to molecules, Debye [10] developed a theory of polar molecular orientation which explained many apparent irregularities in the dielectric constants of fluids. The rotation of the polar molecules under alternating stress gives an additional contribution to the dielectric polarization which is inversely proportional to the absolute temperature. Because of the finite time of relaxation of the molecules in liquids, resulting in an increasing frictional restriction of orientation with increasing frequency, the theory predicts a behavior of the type (2) and (3) for polar liquids. The absorption constant, h_D, depends on the concentration and moment of the polar molecules and on the temperature. The relaxation time is

$$\tau_D = 4\pi\eta a^3/kT, \quad (6)$$

where η = coefficient of inner viscosity; a = radius of polar molecule $\sim 3 \times 10^{-8}$ cm.; k = Boltzmann constant = 1.37×10^{-16} cal. For liquids, the viscosity $\eta \sim 0.01$ to 10 poises, and the frequencies for power factor maxima are in the upper radio frequency range. The best of the early experimental verifications of this anomalous dispersion and energy absorption is that of Mizushima [11] on alcohols and glycerin at 5×10^6 to 10^8 c.p.s. To avoid molecular association, Johnstone and Williams [12] studied polar materials dissolved in a heavy non-polar oil at 25° C. and found the effect above 10^7 c.p.s. Since the frequencies for orientation power factor

maxima are so high for liquids, the contribution at power frequencies is negligible, as shown by Hamburger.[13]

If substances were used such that high viscosity values of 10^6 poises and more are attained on lowering the temperature, it would seem that orientation power factor maxima could be shifted to audio and power frequencies. This was first proposed by Kitchin [14] for the rosin and oil-rosin mixtures studied by him. Kitchin and Müller [15] also showed a close correlation between the disappearance of the Kerr effect and the anomalous dispersion, eq. (3), at 60 c.p.s. as well as at radio frequencies. Kirch and Riebel [16] reached the same conclusion. Gemant,[17] however, contended that there are two power factor—frequency maxima, the one at low frequencies being an inhomogeneity effect and the other at high frequencies being an orientation effect. Bormann and Gemant [18] presented data taken at 60 c.p.s. on substances dissolved in oils which led them to the same conclusions. The suggestion is also presented in Gemant's excellent treatise on dielectrics.[19] Against this view are the results of Morgan and White [20, 21] who made complete frequency studies of rosin and ethyl abietate and also several glycols. These studies showed that power factor maxima can shift continuously from 10^6 to 10 c.p.s. The work of Errera [22] on ice indicates that orientation maxima can take place at audio frequencies for non-insulators at least.

Since all theories leading to a negative exponential relaxation function (1) result in the same type of a.c. behavior (2) and (3), it is impossible to state the cause of an observed curve from an analysis of its shape. This has been recognized by Whitehead [23] and others. Moreover, it can be shown that even the variations of the time constants, τ_W and τ_D, with temperature change are the same. The time constants are proportional to the viscosity since both the translational mobility of the ions in the inhomogeneity theory and the rotational mobility of polar molecules in the Debye theory are inversely proportional to the viscosity.

II. PURPOSE OF THE PRESENT WORK.

It is apparent that the only way to determine the frequency ranges over which the two mechanisms can con-

tribute is to make a study of a non-polar material alone over extended ranges of temperature (viscosity) and frequency, and then to add to this material small known amounts of pure polar substances and see in which ranges the new effects occur. While much evidence has been presented for the existence of the Debye mechanism at low frequencies, it has all been obtained with materials of unknown composition or with concentrated solutions of polar substances which lead to molecular association. The procedure outlined above eliminates these difficulties, and it is the principal purpose of this paper to present such a study. It has been found that the ionic effects are confined to the low frequency range, that the power factor maxima due to the orientation of simple polar molecules are confined to frequencies above 10^7 c.p.s. at ordinary temperatures, and that larger associated or polymerized polar aggregates probably account for the power factor maxima which shift continuously from high to low frequencies as observed in [8, 9, 14, 20]. Study of the nature of the conductivity and other ionic effects has been facilitated through the use of organic acids for the polar substances. Short time d.c. studies have been made to supplement the a.c. studies and these make possible a quantitative study of the variation of the inner viscosity with temperature.

III. APPARATUS AND PROCEDURE.

The measuring apparatus is described in a separate paper.[24] Power factor and dielectric constant measurements were made at frequencies of 65 to 5,000 c.p.s. by means of a double shielded series resistance bridge with Wagner ground, while similar measurements were made at 15,000 to 7,200,000 c.p.s. with a resonance-substitution circuit with vacuum tube voltmeter. The power factor sensitivity for the bridge is usually 0.00002 or better, and for the r.f. circuit is usually 0.00005 or better. The dielectric constant can be obtained to within 0.15 per cent. Short time d.c. studies were made with the amplifier-oscillograph developed by Waldorf,[25] and long time conductivities were measured by means of a sensitive d.c. galvanometer. The conductivity sensitivity is 5×10^{-15} mho cm.$^{-1}$ per mm. for the former and 4×10^{-18} mho cm.$^{-1}$ per mm. for the latter. The temperature range studied was

2.9° C. to 90° C. and the temperature was maintained to within 0.1° C. during frequency runs. A gold-plated measuring cell was constructed for use in all of the above circuits. The samples were melted and mixed under vacuum in a separate container and admitted to the measuring cell under vacuum. After solidification of the sample, nitrogen was admitted to atmospheric pressure. This procedure removes air and moisture from the samples, and prevents deterioration before and during the measurements.

IV. THE SPECIMENS.

The non-polar material used in these experiments is a mixture of equal parts by weight of two paraffins of the imported, filtered type. The melting points of the individual paraffins are 68–72° C. and 40–42° C., and the mixture passes gradually from a liquid to a mushy state, a slight whitening appearing at 67° C. The cooling curve shows only a slight change at this cloud point and no other decided irregularities. The viscosity increases gradually until at 50° C. an impression can be maintained, at 35° C. the mixture is quite stiff although still workable with the fingers, at 20° C. it is apparently very hard. The viscosity-temperature curve is given subsequently. This material has the following advantages: (1) it is almost completely free of polar impurities; (2) high values of viscosity are attained at ordinary temperatures; (3) the viscosity and density changes are sufficiently gradual to allow experimental investigation. A complete study was made on this material alone as specimen 1. In order to check some very small power factor maxima, another sample was studied as specimen 2. A further investigation of the nature of these maxima led to the study of samples of the individual paraffins and these were designated as specimens 5 and 6.

Specimen 3 consisted of a 3 per cent. (by weight) solution of phenol, C_6H_6O, M. P. 41° C., in the paraffin mixture. Phenol is a good example of a small polar molecule having an average value of electric moment, 1.70×10^{-18} e.s.u.,[26] and it is obtainable in a very pure state. The anomalous dispersion of a solution of a polar substance in a non-polar solvent may be calculated from the equations given by

Debye [10]

$$[(\epsilon_1 - 1)/(\epsilon_1 + 2)][(M_1x_1 + M_2x_2)/\rho] = P_1x_1 + P_2x_2, \quad (7)$$

$$P_1 = P_{01} + \mu^2/1.625 \times 10^{-40}T, \quad (8)$$

and the equation

$$[(\epsilon_0 - 1)/(\epsilon_0 + 2)][(M_1x_1 + M_2x_2)/\rho] = P_{01}x_1 + P_2x_2, \quad (9)$$

where ϵ_1 and ϵ_0 are the dielectric constants of the mixture at zero and infinite frequencies, respectively; M_1 and M_2 are the molecular weights, x_1 and x_2 the mol fractions, and P_1 and P_2 the polarizations of the solute and solvent, resp.; and P_{01} is the polarization of the solute at infinite frequency. If eq. (9) is subtracted from eq. (7) and $P_1 - P_{01}$ substituted from eq. (8), and if the weight fractions X_1 and X_2 are introduced in place of the mol fractions, one obtains the relation

$$\frac{\epsilon_1 - \epsilon_0}{(\epsilon_1 + 2)(\epsilon_0 + 2)} = \frac{1}{3} \cdot \frac{\mu^2}{1.625 \times 10^{-40}T} \cdot \frac{\rho X_1}{M_1}. \quad (10)$$

This allows the dispersion for the mixture, $\epsilon_1 - \epsilon_0$, to be calculated in terms of known solute and mixture quantities. Since no solvent quantities are involved, the relation (10) is a useful one in dispersion experiments where the molecular weight of the solvent is not known. In the present case, $\mu = 1.70 \times 10^{-18}$ e.s.u., $X_1 = 0.03$, $\rho = 0.815$ g./cc., $\epsilon_1 = 2.09$, $T = 331°$ K., so that $\epsilon_1 - \epsilon_0 = 0.080$. The power factor maximum corresponding to this, as calculated from the general equation

$$\sin \delta_{max} = (\epsilon_1 - \epsilon_0)/(\epsilon_1 + \epsilon_0) \quad (11)$$

is 0.018, a good value for experimental investigation.

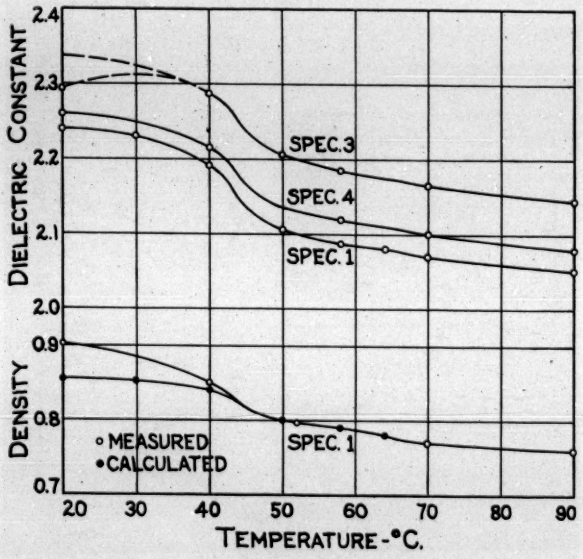
Specimen 4 consisted of a 10 per cent. solution of very pure stearic acid $C_{18}H_{36}O_2$ obtained from Prof. E. E. Reid. This is an example of a polar molecule which is considerably larger than the phenol molecule. A moment value of 0.9 $\times 10^{-18}$ e.s.u. was estimated from values for the lower straight chain acids, and, on solving eqs. (8), (9), (10), (11), the power factor maximum is found to be 0.006.

V. RESULTS.

A. Specimens 1–6.

The density-temperature curve of the solvent alone, presented in Fig. 1, shows the gradual change in density which obtains for the mixture of paraffins. The dielectric constant-temperature curve varies correspondingly. In fact, the varia-

FIG. 1.



Variation with temperature of the dielectric constant at 5,000 c.p.s. and the density.

tion of the effective density of the solvent in the cell may be calculated from this curve, through the use of the relation

$$\rho_{eff} = K(\epsilon - 1)/(\epsilon + 2). \qquad (12)$$

These calculations show that because of the gradual contraction, the material completely fills the cell for temperatures down to about 43° C. Below this, the cell is not completely filled, due evidently to the formation of voids. The densities

of specimens 3 and 4 vary in a similar manner to that of specimen 1, but are about 1 per cent. higher. The higher values of dielectric constant obtained for these specimens in the liquid and amorphous states are due mostly to the orientation of the polar molecules as calculated from eq. (10), although about 0.010 of the difference is caused by the increased densities. At temperatures below 40° C. there is evidently a partial crystallization of the polar solute as indicated by the smaller differences in the dielectric constant curves. This effect will be discussed later in some detail.

FIG. 2.

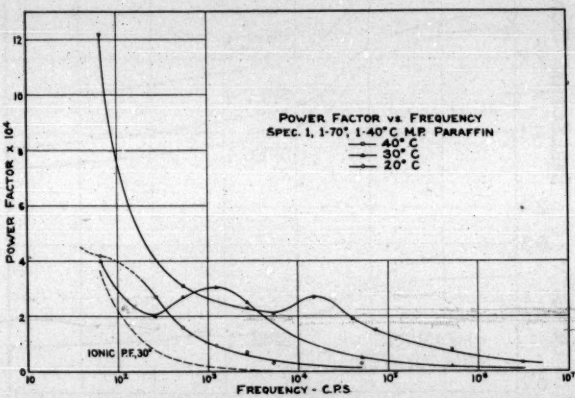
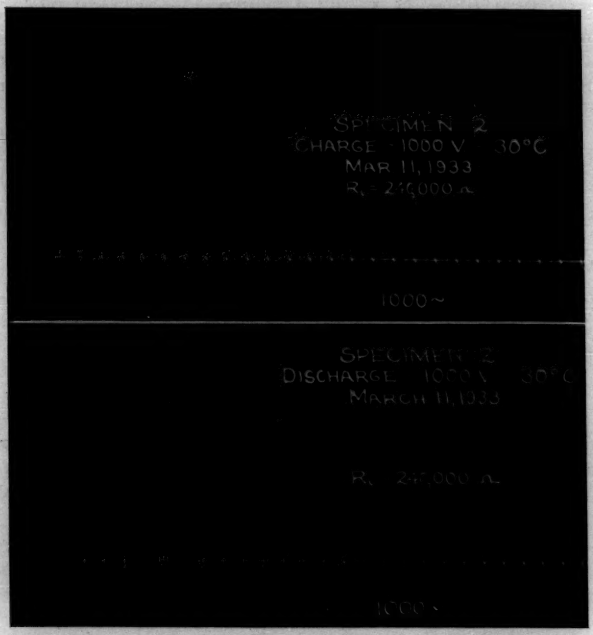


Figure 2 shows the variation of power factor *vs.* frequency at 20° C., 30° C., and 40° C. for specimen 1, the paraffin solvent alone. These power factor curves are made up of two parts: (1) a component caused by ionic phenomena, which decreases as the reciprocal of the frequency; (2) a power factor maximum of value 0.00029. This maximum, the smallest of this type yet reported, was first observed at 30° C. at about 1,300 c.p.s. Raising the temperature to 40° C. shifts the maximum up to about 16,000 c.p.s., while lowering the temperature to 20° C. shifts it down to about 100 c.p.s., a change of frequency of about 13-fold in each case. Above

40° C. the maximum disappears. These curves are somewhat broader than the theoretical curve, eq. (2), but not greatly so. The anomalous dispersion corresponding to this maximum is less than 0.002 which is within the limit of accuracy of the measurements.

FIG. 3



Ionic polarization absorption and short time conduction in paraffin at 30° C.

The ionic losses increase rapidly as the temperature rises. At 70° C. and above (liquid state) they are entirely due to conduction, but with the gradual solidification below 67° C., ionic polarization appears along with the conduction. Figure 3 presents oscillograms showing the charge and discharge curves at 30° C. The time constants of the absorption curves

are so large that the power factor maxima corresponding to them lie considerably below 65 c.p.s. Therefore, above 65 c.p.s., the power factor contribution from this source varies inversely with the frequency (see eq. 2) or the same way as that due to conductivity, δ_λ, which is

$$\delta_\lambda = \lambda/8.85 \times 10^{-14}\omega\epsilon. \qquad (13)$$

The oscillograms show the appreciable conduction (charge minus discharge) current which greatly exceeds the long time value, the behavior shown by liquids. Values of initial and final conductivities at various temperatures are given in Table I.

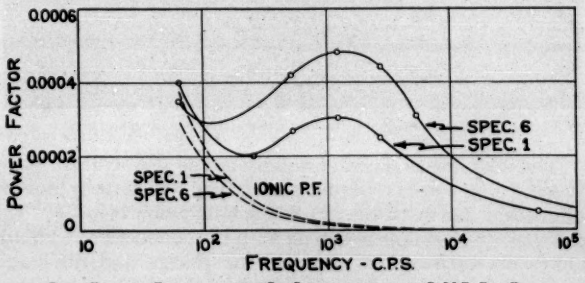
TABLE I.

Initial and Final Conductivity in Paraffin.

Temperature, ° C.	Unit: mho cm.$^{-1}$ × 10^{-17}.		
	λ_i.	λ_f.	λ_i/λ_f.
90	155,000	10,700	15
70	79,000	840	94
64	50,500	470	108
58	26,000	130	200
50	10,500	33	320
40	3,300	7.8	430
30	1,900	3.6	530

The power factor of the 40° M.P. paraffin alone, specimen 6, passes through a maximum of value 0.00047 at about the same frequency as that for the mixture, as shown by Fig. 4.

FIG. 4.

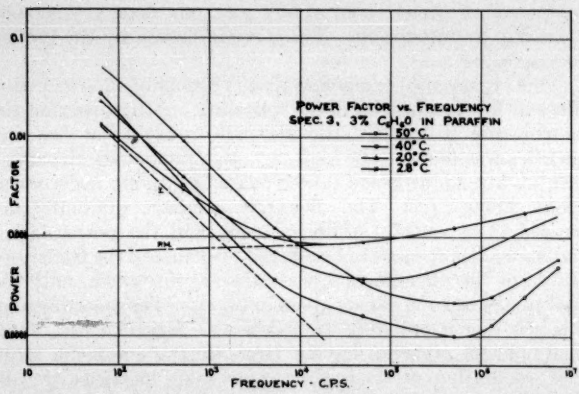


Power Factor *vs.* Frequency at 30° C. Spec. 1, 1–70°, 1–40° C. M.P. Paraffins. Spec. 6, 40° C. M.P. Paraffin.

No maximum was observed for the 70° M.P. paraffin alone. Since the mol fraction of the 40° paraffin is about 62 per cent., the effect of mixing the paraffins on the power factor maximum is simply one of dilution of an impurity already present in the 40° paraffin and is not a layer dielectric effect. It will be shown later that this impurity is probably in the form of polar aggregates.

The power factor-frequency curves at 50° C., 40° C., 20° C., 2.8° C., for specimen 3, 3 per cent. phenol, have been plotted in Fig. 5 with logarithmic scales in both power factor

FIG. 5.



and frequency. For these coördinates, the hyperbola representing the variation of the power factor due to ionic effects becomes a straight line of negative slope, and also the rising parts leading to power factor maxima are straight lines of positive slope. In analyzing these curves, it is necessary to remember that they are the combined results of as many as four contributing phenomena.

Adding the phenol produces two effects: (1) the magnitudes of the ionic phenomena, as indicated by the power factor at low frequencies, are greatly increased because of the partial dissociation as an organic acid; (2) power factor

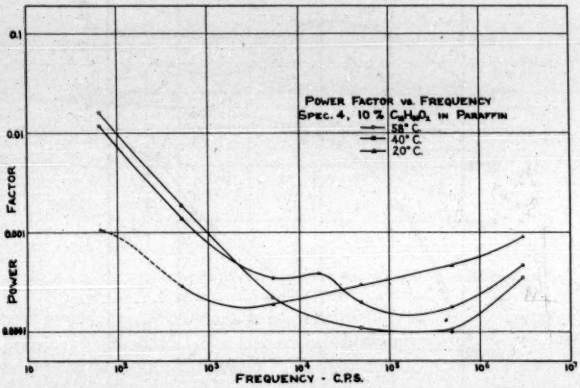
maxima are found at high frequencies due to the orientation of the polar molecules. Other types of polar molecules, such as chlorbenzene, would produce only the second effect. It is seen that even though the temperature is lowered to 2.8° C., these orientation maxima remain above 7.2×10^6 c.p.s. and only the rising portions can be observed. Lowering the temperature, and hence greatly increasing the apparent viscosity, seems to broaden the maxima, as seen from the decreasing slopes of the curves. The tendency to shift to lower frequencies is slight. The 2.8° C. curve may be broken up into two components: (1) a hyperbolic decreasing component due to ionic effects; (2) a very gradually rising component of about 0.0007 at 60 c.p.s. and 0.0022 at 7,200,000 c.p.s. due to orientation. These are indicated by the broken curves in Fig. 5.

One observed phenomenon that is probably an orientation effect at low frequencies is the following. After lowering the temperature to 20° C., the dielectric constant at low frequencies was found to be high, 2.7, and anomalous dispersion with an attendant broad power factor maximum occurred at about 5,000 c.p.s. The dielectric constant gradually decreased to a constant value of 2.286 and the power factor maximum disappeared in two days. Because of the transitory nature of the phenomenon, the data are not given, only the final curve for 20° C. being given in Fig. 5. The mechanism of this behavior is probably the following. Upon cooling, some small phenol crystals, having large electric moment, form. The orientation of these polar aggregates increases the dielectric constant at low frequencies, but since the dipoles are of larger than molecular size, they are restricted from orientation at a relatively low frequency and give rise to a power factor maximum there. As the crystals continue to grow, they become so large that they cannot rotate at all and the whole effect disappears. The dielectric constant data indicate that about half of the phenol crystallizes out in this manner, the value after crystallization being only 0.05 above that for the solvent alone as against 0.10 at higher temperatures. On pouring the material into a glass tube, one can observe the phenol crystallizing out in streaks. Increased local dissociation in these streaks results in ionic effects which increase with

time. The ionic phenomena will be discussed later under comparison of results.

It was thought that by increasing the size of the polar molecules in comparison with the spaces between solvent molecules, restriction of molecular orientation would occur at much lower frequencies. The considerably larger stearic acid molecule was tried for this reason. However, the data for this specimen presented in Fig. 6 show a behavior similar to

FIG. 6.



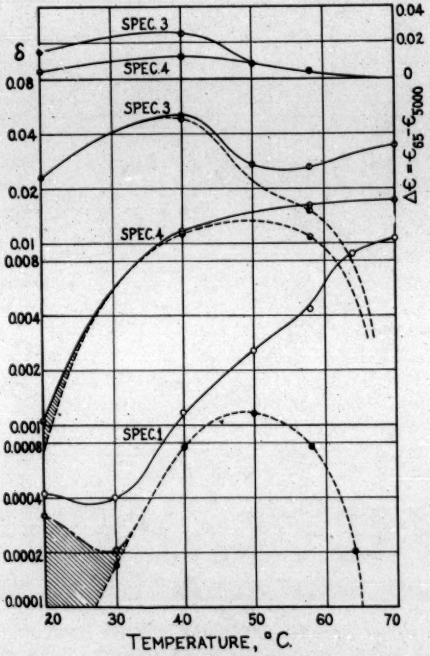
that for the phenol specimen. The ionic effects are somewhat smaller for the stearic acid. The 40° C. curve is especially interesting. It is made up of three parts: (1) at low frequencies, due to ionic polarization; (2) at high radio frequencies, due to polar molecular orientation; (3) a power factor maximum capable of being shifted from high to low frequencies as observed in the solvent alone. This maximum was masked in the phenol specimen by the large ionic effects.

B. Comparison of Results.

The behavior of the ionic phenomena may be seen more clearly from Fig. 7 which presents the power factor at 65 c.p.s. *vs.* temperature for specimens 1, 3, and 4. Short time d.c. measurements were made at all points noted and the curves

analyzed. The power factor contributions due to ionic polarizations absorption are shown by the dotted curves, and the differences are due to conduction. It can be seen that the absorption contribution goes through a maximum in all

FIG. 7.



Power factor, δ, at 65 c.p.s. *vs.* temperature curves of specimens 1, 3, and 4. The contributions caused by ionic polarization (dotted curves), polar aggregates (hatched areas), and conduction (differences) are shown. The increment in dielectric constant, $\Delta\epsilon$, caused by ionic polarization is also shown.

specimens, being zero in the liquid state, low at low temperatures, and high at 40° C. where the solidification of the paraffin of lower melting point occurs. It is only when the concentration of ions is extremely large and the degree of

heterogeneity great, as in specimen 3, that the *resultant* curve goes through a maximum. Moreover, it is to be noted that increasing the temperature does not shift these maxima to higher frequencies (Fig. 5). The effect of temperature is merely that of a change in the degree of inhomogeneity, p, eq. (4), through changes in the structure of the material, and not a change in the time constant which remains large throughout. The values of the time constants of the absorption curves are given in Table II. These are effective values,

TABLE II.

Effective Time Constants of Ionic Polarization Absorption Curves.

Temperature ° C.	Time Constants in Milliseconds.		
	Specimen 1.	Specimen 3.	Specimen 4.
2.9		7.5	
20	3.5	12	8
30	3		
40	7	10	13
50	4		
58	5	15	29
64	8		

the curves being made up of a number of the elementary negative exponential curves, some of which have longer time constants and some shorter. The values do not vary greatly with temperature change. Below 5,000 c.p.s. the ionic polarization in specimens 3 and 4 is sufficient to give a measurable contribution to the dielectric constant. The values of $\epsilon_{65} - \epsilon_{5,000}$ are plotted in Fig. 7. The increments in dielectric constant at various temperatures and also those at various frequencies are roughly proportional to the ionic polarization power factor.

Table III presents values of the initial conductivity, λ_i, and the final conductivity, λ_f, for the three specimens at 58°, 70°, and 90° C. By subtracting the final conductivities from the initial conductivities, the quantities designated as the true short time conductivities, λ_s, are obtained. It is evident that although great increases in the final conductivities are brought about on adding organic acids, the true short time conductivities increase little, if at all. The true short

TABLE III.

Effect of Organic Acids on Conductivity.

Specimen 1. Paraffin.
Specimen 3. 3 per cent. phenol in paraffin.
Specimen 4. 10 per cent. stearic acid in paraffin.
Unit of Conductivity: mho cm.$^{-1}$ $\times$ 10^{-15}.

Temp.	Initial λ_i.			Final λ_f.			True Short Time $\lambda_s = \lambda_i - \lambda_f$.		
	Sp. 1.	Sp. 3.	Sp. 4.	Sp. 1.	Sp. 3.	Sp. 4.	Sp. 1.	Sp. 3.	Sp. 4.
58° C...	260	820	400	1	540	140	260	280	260
70° C...	790	2,650	1,300	8	1,700	360	780	950	940
90° C...	1,540		2,400	110		900	1,430		1,500

time conductivity is an important basic quantity, more so than the total initial conductivity, as will be seen from subsequent discussion.

C. Viscosity.

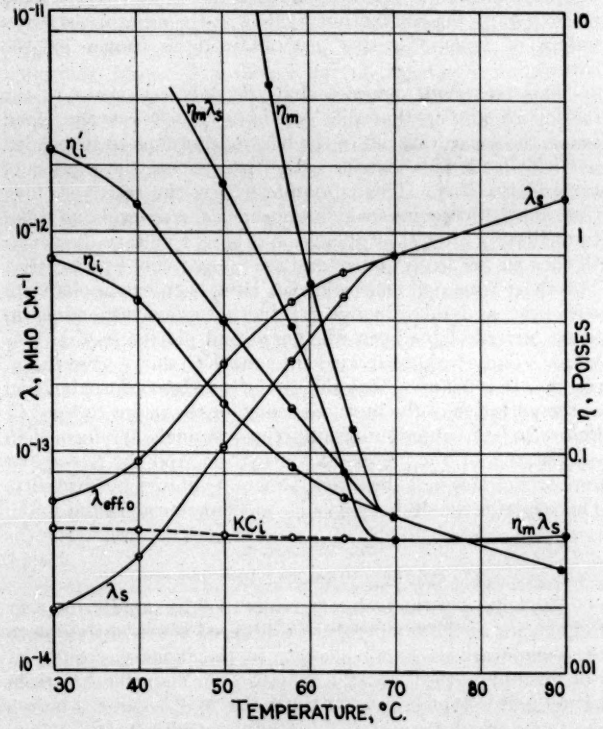
The viscosities of the specimens in the liquid and amorphous states were obtained by a Saybolt viscosimeter and the readings converted to poises. The viscosity-temperature curve for specimen 1 is given in Fig. 8. The values for specimens 3 and 4 are very nearly the same. The sharp rise in this macroscopic viscosity curve below the cloud point at 68° C. is to be noted.

It has been shown by Whitehead [5] that the product of the effective conductivity, λ_0, and the viscosity, η, for a large number of oils, is essentially unaffected by temperature over the range 25°–70° C. It is shown in Fig. 8 that this also holds for the paraffin in the range 70°–90° C. Since the mobility of ions varies inversely as the viscosity and since the conductivity is proportional to the product of the mobility and the number of ions per unit volume, the product, $\eta \cdot \lambda$, is a quantity proportional to the number of ions per unit volume. The fact that the product is constant over a considerable temperature range, leads to the conclusion that the degree of dissociation is independent of temperature.

This fact makes it possible to gain an idea of the variation of the inner viscosity, the viscosity restricting the motion of small particles, in the amorphous and solid states. For a liquid, the inner viscosity evidently varies in about the same

way as the macroscopic viscosity does. Below the cloud point, however, the product $\eta \cdot \lambda$ rises abruptly, which indicates that the macroscopic viscosity is increasing much more

FIG. 8.



Viscosity and Conductivity of Paraffin. λ_s = true short time conductivity; $\lambda_{eff.o}$ = effective conductivity at zero time; η_m = macroscopic viscosity; $KC_i = (\rho/\rho_{75})(\eta_m\lambda_s)_{75} \backsim$ concentration of ions; $\eta_i' = KC_i/\lambda_s$, $\eta_i = KC_i/\lambda_{eff.o}$ = inner viscosity.

rapidly than the inner viscosity. This is the same phenomenon as that observed in the classical experiment in physical chemistry,[27] which shows the high mobility of ions

in a gel. To find the inner viscosity, η_i, it is assumed that the degree of dissociation, which is later shown to be complete, remains unchanged in the solid state. Then the concentration of ions increases only the small amount due to the higher densities, as shown by the KC_i curve in Fig. 8. By dividing this curve by the conductivity values in the amorphous state, values of inner viscosity are obtained as shown by the curve η_i'.

This treatment assumes that the only resistance to the motion of ions is that due to viscosity. Below the cloud point, the separating out of the heavier paraffins as suspended particles leads to a barrier action preventing the motion of some of the ions. This is manifested by the relatively long time absorption curves which appear in the amorphous state. Immediately after the application of direct voltage, however, all the ions are free to move and are limited only by viscosity. The short time d.c. charge curves have been extrapolated to zero time and the effective conductivities corresponding to these currents have been calculated and plotted in Fig. 8 as $\lambda_{eff.\ 0}$. These values divided into the KC_i curve give the η_i curve. It is believed that this curve is a close approximation to the variation of the inner viscosity for the range 40°–90° C. Below 40° C., numerous conducting channels are formed in the paraffin by the increased contraction, and the passage of ions occurs through these and so is not limited by viscosity. This explains the decreasing slope of the η_i curve below 40° C.

VI. DISCUSSION.

A. Power Factor Maxima Due to Dipole Orientation.

The failure of the Debye maxima to shift rapidly to lower frequencies as the temperature is lowered is evidently due to the comparatively small increase in the inner viscosity, η_i. For example, at 50° C., the macroscopic viscosity has risen to 165 poises, which is 3,200 times the 70° C. value, whereas the inner viscosity at 50° C. is only 3 times its 70° value. Moreover, dispersion experiments on liquids, such as water, indicate that even there the inner viscosity may be only about 1 per cent. of the macroscopic value. A number of writers have made statements to the effect that the inner viscosity in very viscous materials is probably less than the

apparent value, and the conductivity data and analysis presented above give quantitative evidence of this.

Oncley and Williams,[28] working in the range 156 to 17.5 meters and at temperatures of 25° C. and 10° C., have measured a number of polar materials in various solvents of viscosities of 100 poises and greater, yet no appreciable dispersion was observed in the cases where the solute existed in molecular form. The power factor measurements in the present experiments indicate a dispersion which is too small to measure as such, the greatest values being about 0.001.

The slope of the rising portion of the theoretical monodisperse log power factor-log frequency curve is unity. The fact that the slopes of the experimental curves become less and less with decreasing temperature shows definitely that the curves are becoming increasingly broad. That is, as the temperature is lowered, the relaxation times, τ, of a small but increasing number of the molecules increases, but τ for most of the molecules remains small. From eq. (6), τ is proportional to ηa^3. It seems probable that a range of values of τ can occur not only through a variation in dipole radius caused by association, but also through a variation of the viscosity restricting the individual molecules caused by differences in the surrounding medium. The broadness of the power factor curves, and hence the range of distribution of η, is small for concentrated solutions of polar material and increases with decreasing concentration as shown by the results of White and Morgan [21] together with the results presented here.

It appears that the viscosity may be regarded as a function of the particle radius. For a large sphere, η_i assumes the macroscopic value of viscosity. For an electron regarded as an infinitesimal sphere, the absence of a viscosity effect on the electronic conduction in very pure hydrocarbons, as shown by Jaffé,[1] indicates that η_i is infinitesimally small. Finally, for an ion or a small polar molecule, an intermediate value of η_i is encountered. In the Millikan oil drop experiments, departures from Stoke's equation for translational velocity were observed, and these were found to be a function of the ratio of particle radius to the intermolecular distances of the medium. Instead of correcting Stoke's equation for this

ratio, the effect may be taken into account by regarding the correction as applying to the viscosity. The latter method may be preferred by workers in dielectrics since they have already introduced the concept of a lower inner viscosity for dipole orientation. The viscosity may thus be considered as $\eta_i = \eta_i(a/l)$, where l, the intermolecular distance, depends on the solvent and also varies within the solvent.

A number of investigators [14, 16, 28] have shown that rosin even in dilute solution will cause dispersion at the lower frequencies. It seems that the condition for dispersion at frequencies less than 10^7 c.p.s. and temperatures greater than 0° C. is that the polar material be polymerized or associated. In either case, the radius, a, is large and the relaxation time is increased through the larger values of $\eta_i(a/l)$ in addition to the effect of the a^3 factor. The small power factor maxima in the paraffin alone, Fig. 2, are therefore probably due to the orientation of polar aggregates of large radius. It is certain that they are not due to the orientation of simple polar molecules (Figs. 5 and 6), to ionic polarization (Fig. 7), or to any inhomogeneity produced by mixing paraffins (Fig. 4).

The broadening of any power factor-frequency curve can be represented by a distribution of values $h(\tau)$ in eq. (2). It is interesting to note that the area under the p.f. *vs.* $\ln f$ curve remains proportional to the total dispersion. The power factor at any frequency

$$\delta(\omega) = \int_0^\infty \frac{\omega\tau}{1 + \omega^2\tau^2} h(\tau)d\tau. \qquad (14)$$

Substituting $\ln \omega\tau = u$, the area under the $\delta(u)$ curve is

$$\int_{-\infty}^{\infty} \delta(u)du = \int_{-\infty}^{\infty} du \int_0^\infty \tfrac{1}{2} \operatorname{sech} u \cdot h(\tau)d\tau. \qquad (15)$$

Integrating first for u (τ constant and ω variable), and then for τ,

$$\int_{-\infty}^{\infty} \delta(u)du = \int_{-\infty}^{\infty} \delta(\ln f)d(\ln f)$$

$$= \frac{\pi}{2}\int_0^\infty h(\tau)d\tau = \frac{\pi}{2}\frac{\epsilon_1 - \epsilon_0}{\epsilon_0}. \qquad (16)$$

The application of power factor measurements to dispersion phenomena has also been dealt with in the companion paper.[24]

B. Conductivity.

The results presented in Table III show that the organic acids ionize in insulating liquids and the ions thus formed contribute greatly to the final conductivity, although the effect on the true short time conductivity is much less and perhaps nil. This means that the true short time conductivity is caused by ions other than organic ions. The fact that the degree of dissociation for this type of ion is essentially independent of temperature has already been pointed out as a consequence of the constancy of the $\eta \cdot \lambda_s$ curve. To be independent of the ionization constants, which increase rapidly with temperature increase, the materials must be completely ionized throughout the temperature range. From the Ostwald dilution law,[29] this requires that the ratio of concentration to ionization constant be much less than one. The final conductivity, however, increases much more rapidly than the initial as the temperature rises, as shown by Whitehead [5] and by the values of λ_i/λ_f in Table I. This means that $\eta \cdot \lambda_f$, and therefore the ionization of organic materials, increases with temperature increase. The ratio of concentration to ionization constant of the organic materials is consequently much greater than that for the material producing the short time ions even where organic material is not purposely added. This difference can be explained by a much greater ionization constant for the short time ions which would mean that they are inorganic (the ionization constant of a material is much less in a dielectric solvent than in water as shown by Gemant [19]). These conclusions as to the nature of the ions causing conduction in oils have been previously reached by Herzfeld [30] from an analysis of the potential distribution curve of an oil.

C. Ionic Polarization Absorption.

The long time absorption curves and the attendant high power factor in the low frequency range may be regarded as the result of a kind of inhomogeneity mechanism. Actually the mechanism is very much more complicated than those de-

veloped by Maxwell and Wagner, and it seems preferable to regard the phenomena from the microscopic point of view. The action is due to the restricted motion of ions resulting in ionic polarization. Just below the cloud point this restriction is due to the presence of suspended non-conducting particles, while in the solid state it is due to the finite lengths of conducting channels. The restraining force in the first case is viscous, and in the latter case largely adsorptive. The time constant of the absorption depends on this restraining force and on the path length. The restraining force evidently does not vary greatly with the temperature, Fig. 8. As shown by Table III, the time constant may actually decrease with temperature decrease in direct contradiction to the Wagner development. There also appears to be an effect of ion size as seen by comparing the values for specimens 1, 3, and 4, most of the ions in 1 being inorganic. The time constant may be expected to decrease with increasing voltage. While this effect can be observed in the data of Whitehead and Marvin,[31] it is probably masked to a great extent due to the existence of the large number of exponential relaxations of different time constants. Because of the small effect of temperature on the time constant, this mechanism gives power factor maxima restricted to the very low frequency range, unless a high conductivity layer is deliberately introduced, see Race.[32] The absorption constant, h, depends on the concentration of ions as shown in Fig. 7. This has also been shown by Whitehead [5] for the case of impregnated paper. The dependence of h on the final conductivity has long been noted, see Whitehead and Marvin.[31]

VII. SUMMARY.

1. Measurements of dielectric constant and power factor have been made over the frequency range, 65 to 7.2×10^6 c.p.s. and temperature range 2.8° C. to 90° C. on paraffin and on both phenol and stearic acid in dilute solution in the paraffin. Short time d.c. studies have also been made over the temperature range. Three types of dielectric absorption leading to power factor maxima, and two types of ionic conduction have been studied.

2. The power factor maxima due to the orientation of

simple polar molecules in dilute solution remain above 7.2×10^6 c.p.s. for all temperatures in these experiments although the apparent viscosity attains very high values. Lowering the temperature decreases the frequency for maximum power factor only slightly and its principal effect is to broaden the power factor curve considerably. A small orientation loss may be present at 60 c.p.s. at 20° C. and below. The broadening may be due to a variation of the inner viscosity within the medium as well as to the presence of dipoles of different sizes.

3. The power factor maxima due to ionic polarization or inhomogeneity effects found in the amorphous and solid states remain below 60 c.p.s. The magnitude of the effect is proportional to the concentration of ions present. The behavior is much more complex than that predicted by simple inhomogeneity theories. A tendency for the time constant to increase with rise in temperature and with increase in ion size is observed.

4. The failure of these two types of power factor maxima to shift over extended ranges of frequency with temperature change is due to the failure of the inner viscosity to increase rapidly in the solid state, thus giving only small changes in the rotational mobility of polar molecules in the one case and in the translational mobility of ions in the other. Quantitative results for the variation of inner viscosity with temperature are obtained from the reciprocals of the short time conductivities.

5. In between the high and low frequency ranges, and capable of being shifted from one to the other with essentially unchanged magnitude, is a third type of power factor maximum caused by the orientation of larger associated or polymerized polar aggregates. The viscosity restricting the motion of a particle may be thought of as being a function of the particle radius compared with intermolecular distances.

6. The true short time conductivity is defined as the difference of the initial and final conductivities. The true short time conductivity is largely caused by ions arising from complete dissociation of inorganic material, whereas the final conductivity is caused by organic ions arising from partial dissociation of organic material.

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THE DYNAMICS OF MOLECULAR CRYSTAL LATTICES. I. NEON.

BY

V. DEITZ.*

INTRODUCTION.

In the application of the third law of thermodynamics to the study of chemical reactions it is important to have an extensive knowledge of the heat capacity of substances at low temperatures. Because of the experimental difficulties involved, the accumulation of this data has been rather slow, and for this reason it is highly desirable at the present time to have available methods for calculating heat capacities at low temperatures on the basis of theoretical considerations. Born and his associates have developed a very satisfactory theoretical treatment for crystals of the ionic type, but little work has been done on crystals in which the vibrating units consist of molecules, despite the preponderance of molecular crystals in nature.

In many instances there is additional interest in knowing something about the molecular crystal forces because these forces play an important part in determining the chemical behavior of the compounds. This is true for organic compounds, especially for those of biochemical interest. Although the Van der Waals forces are relatively weak between a pair of atoms, which are constituent atoms of different molecules, for large molecules like the waxes and sugars, the total of the Van der Waals force over the whole molecule may be very large. For example, the energy for removing a wax molecule from its place in the crystal lattice is of the order of magnitude of several hundred kilocalories. Furthermore, forces distributed over so large an area lead to a more or less independent behavior of some particular part of the molecule

* Research Fellow, The Johns Hopkins University, 1932–33; National Research Fellow, The University of Illinois, 1933–34.

which results in a decrease in those orienting influences which produce a crystalline solid.

It is planned gradually to lead up to considerations of these larger molecules by first studying the simplest of molecular lattices, namely, those of the rare gases, Ne and A. Then in the following paper there will be discussed a diatomic example, solid N_2 of the α modification. In a later paper the results for CH_4, C_2H_6, and *n*-hexane as well as some general considerations for organic substances will be presented.

LATTICE ENERGY CONSIDERATIONS.

By definition the lattice energy, Φ, of a molecular crystal is simply the energy change at 0° K. for the reaction M (crystal) $\rightarrow$ M (gas) and may be given by the following equation:

$$\Phi = \tfrac{1}{2}(-A + B) + E_0 = -\Delta H_{\text{Sub.}}, \qquad (1)$$

where A is the potential energy due to the forces of attraction; B is that due to the forces of repulsion; E_0 is the zero point energy; and $\Delta H_{\text{Sub.}}$ is the heat of sublimation. London [1] first pointed out that the attraction potential in molecular lattices is due to a resonance potential, arising from the polarization of one atom by the electric field of the others, varying as the inverse sixth power of the distance between the atoms. Later Morgenau [2] showed that an additional smaller term must be added, varying inversely as the eighth power of the distance. The general molecular crystal might also have in addition the electrostatic attraction of the permanent dipoles present and an attraction due to an induction effect of one permanent dipole on the neighbors.

The repulsion potential can be best represented by an exponential law of the type $be^{-r/\rho}$ where b, ρ are constants.

The third term, E_0, in the expression for Φ is the zero point energy. It constitutes an appreciable part for lattices of the lighter mass particles, in fact for neon it is about 33 per cent. of the observed heat of sublimation.[3]

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[1] London, *Zeit. Phys. Chem.*, **B11**, 222 (1930).
[2] Morgenau, *Phys. Rev.*, **38**, 747 (1931).
[3] V. Deitz, *J. Chem. Phys.*, **2**, 296 (1934).

EVALUATION OF THE POTENTIAL CONSTANTS.

The complete lattice energy can now be given by:

$$\Phi_0 = \frac{1}{2}\left[- \Sigma \frac{c_{ij}}{r_0^6} - \Sigma \frac{d_{ij}}{r_0^8} + 12be^{-r/\rho} \right] + E_0$$
$$= - \Delta H_{\text{Sub. per atom}}\ 0^\circ\ \text{K.}, \quad (2)$$

where r_0 is the equilibrium distance between atoms. c_{ij} and d_{ij} are constants [4] related by the expression:

$$d_{ij} = \frac{3}{4} \frac{{c_{ij}}^2}{e^2\alpha}, \quad (3)$$

where e is the charge on the electron and α is the polarizability. The summation is over the whole lattice. The repulsion potential decreases so rapidly with distance that only the immediate twelve neighbors contribute.

Slater and Kirkwood [5] have suggested the following approximation formula for the attraction constant c_{ij}:

$$c_{ij} = (11.25 \times 10^{-24})\alpha^{3/2}n^{1/2}\ \text{erg-cm.}^6,$$

where n is the number of electrons in the external shell. The constant in this expression was determined from the more accurate calculations for hydrogen and for helium atoms. In Table I a comparison is shown between the values calculated from this equation and values which have been obtained from the more precise theoretical calculations noted. The agreement is fair except in the case of the negative ions where if n were taken to be 4 (more nearly the calculated electron number) the agreement would be better, as shown in column 6.

In view of the lack of good agreement the semi-empirical method of Morgenau [6] for calculating c_{ij} from spectroscopic data has been applied to neon and argon. To apply this method one must know the energy levels and the relative intensities of the allowed transitions from the normal state.

Equation (6) of Morgenau's paper can be put into the following form for neon:

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[4] J. Mayer, *J. Chem. Phys.*, 1, 270, 327 (1933).
[5] Slater and Kirkwood, *Phys. Rev.*, 37, 682 (1931).
[6] Morgenau, *Phys. Rev.*, 37, 1425 (1931).

TABLE I.

	$\alpha \times 10^{24}$.	n.	S and K c_{ij}.	Accurate Value c_{ij}.		c_{ij}.
H	0.670	1	6.18×10^{-60}	6.161×10^{-60}	(6)	
He	.205	2	1.48	1.49	(5)	
Na	24.2	1	0.134	0.145	(7)	
Li^+	0.030	2	0.083	0.073	(4)	
Na^+	.182	8	2.47	1.68	(4)	
K^+	.844	8	$.247 \times 10^{-58}$	$.243 \times 10^{-58}$	(4)	
Rb^+	1.42	8	.540	.594	(4)	
Cs^+	2.45	8	1.23	1.52	(4)	
F —in LiF	0.90	8	0.273	0.145	(4)	0.193×10^{-58}
NaF	.98	8	.309	.165	(4)	.218
KF	1.11	8	.373	.186	(4)	.264
RbF	1.18	8	.409	.189	(4)	.289
CsF	1.15	8	.393	.191	(4)	.278
AgF	1.15	8	.39	.19	(4)	.27
Cl—in LiCl	2.95	8	1.61	1.11	(4)	1.14
NaCl	3.09	8	1.77	1.16	(4)	1.25
KCl	3.30	8	1.82	1.25	(4)	1.28
RbCl	3.29	8	1.90	1.30	(4)	1.34
CsCl	3.22	8	1.84	1.29	(4)	1.30
AgCl	3.45	8	2.04	1.33	(4)	1.43
TlCl	3.45	8	2.04	1.33	(4)	1.43
Br—in LiBr	4.06	8	2.60	1.85	(4)	1.83
NaBr	4.29	8	2.83	1.96	(4)	2.00
KBr	4.38	8	2.92	2.06	(4)	2.06
RbBr	4.50	8	3.04	2.15	(4)	2.14
CsBr	4.47	8	3.01	2.14	(4)	2.13
AgBr	4.47	8	3.02	2.08	(4)	2.13
TlBr	4.47	8	3.02	2.08	(4)	2.13
I —in LiI	6.00	8	4.60	3.78	(4)	3.25
NaI	6.24	8	4.98	3.92	(4)	3.52
KI	6.57	8	5.26	4.03	(4)	3.72
RbI	6.65	8	5.46	4.28	(4)	3.85
CsI	6.60	8	5.40	4.24	(4)	3.81
AgI	7.29	8	6.26	4.37	(4)	4.41
TlI	7.29	8	6.26	4.37	(4)	4.41
Ag^+	1.72	10	0.80	0.67	(4)	
Tl^+	3.50	12	2.56	2.68	(4)	
Ne	0.39	8	7.75×10^{-60}	11.405×10^{-60}	*	
A	1.63	8	66.2	67.4×10^{-60}	*	
N	0.87	5	20.4			

* From this paper.

$$\Delta_2 E = -\frac{2.837 \times 10^{-60}}{r^6}\left[\beta^2 \sum_{\alpha}{}' \sum_{\beta}{}' \frac{\phi_\alpha \phi_\beta}{v_\alpha v_\beta (v_\alpha + v_\beta)} + \beta\gamma \sum_{\alpha}{}' \phi_\alpha R_\alpha + .0403\gamma^2\right]. \quad (4)$$

β and γ are constants which may be determined from the two relations

$$\sum_{\alpha}{}' f_{1\alpha} + \int_0^{\infty} \frac{df_{1E}}{dE}\, dE = Z_0,$$

$$\beta \sum_{\alpha}{}' \frac{\phi_\alpha}{v_\alpha{}^2} + \frac{\gamma}{4} = m\epsilon_1{}^2 \left(\frac{2\pi}{eh}\right)^2 \alpha, \qquad (5)$$

where $f_{1\alpha} \equiv$ transition probability from the normal state 1 to α,

$m =$ mass of the electron,

$\epsilon_1 =$ 1st ionization potential of neon,

$v_\alpha = 1 - \frac{\epsilon_\alpha}{\epsilon_1}$ where $\epsilon_\alpha = -E_\alpha$, the energy of state,

$\alpha =$ polarizability.

The distribution of the transition probabilities are assigned as follows; for the continuous region, $\frac{df_{1E}}{dE} = \frac{\gamma}{(1+E)^3}$, for the discrete levels, $f_{1\alpha} = \frac{\beta J_\alpha}{v_\alpha{}^3} \equiv \beta\phi_\alpha$, where J_α is the relative intensity.

$$R_\alpha = \frac{2}{v_\alpha{}^2}\left[\frac{1}{3} - \frac{1}{2v_\alpha} + \frac{1}{v_\alpha{}^2} - \frac{1}{v_\alpha{}^3}\ln(v_\alpha + 1)\right].$$

The data used consider only transitions involving change of the main quantum number. These were taken from Bacher and Goudsmit and from the relative intensity data of Lyman and Saunders.[9]

TABLE II.

	Transition.	Wave Number.	Relative Intensity.
Ground level	$\epsilon_1(2p^6)$	173,930 cm.	
1st transition	$\epsilon_2(2p^5 3s) \rightarrow \epsilon_1$	38,760 cm.	10
2d transition	$\epsilon_3(2p^5 4s) \rightarrow \epsilon_1$	14,770	5
3d transition	$\epsilon_4(2p^5 3d) \rightarrow \epsilon_1$	12,100	3
4th transition	$\epsilon_5(2p^5 5s) \rightarrow \epsilon_1$	7,650	2.5
5th transition	$\epsilon_6(2p^5 4d) \rightarrow \epsilon_1$	6,660	1.5
6th transition	$\epsilon_7(2p^5 6s) \rightarrow \epsilon_1$	4,580	1
7th transition	$\epsilon_8(2p^5 5d) \rightarrow \epsilon_1$	4,426	1
8th transition	$\epsilon_9(2p^5 7s) \rightarrow \epsilon_1$	3,370	.3

[9] Lyman and Saunders, *Proc. Nat. Acad. Sci.*, **12**, 93 (1926).

Using these data the $\Sigma\phi_a = 1.811$ and the summation $\Sigma \frac{\phi_a}{v_a^2} = 2.582$; hence the equations (5) determining β and γ become:

$$1.811\beta + \frac{\gamma}{2} = 8,$$

$$2.582\beta + \frac{\gamma}{4} = 1.652 \qquad \text{and} \qquad \beta = -1.402$$

$$\gamma = +17.08.$$

Evaluating the summations in equation (4) we obtain the result:

$$\Delta_2 E = \frac{-11.405 \times 10^{-60}}{r^6}.$$

Using the equation (3) $d_{ij} = 11.0 \times 10^{-76}$. The summation of the attraction potential over the face-centered lattice of neon is easily computed using the table given by Lennard-Jones and Ingham.[10]

From equation (2) and from the first derivative of potential which must be zero, one obtains the following two relations which determine the two constants ρ and b of the repulsion potential.

$$1/2[-1.663 \times 10^{-13} + 12be^{-r/\rho}] + .098 \times 10^{-13} = -.293 \times 10^{-13}$$

$$\left[+3.198 \times 10^{-5} - 12\frac{b}{\rho}e^{-r/\rho}\right] = 0.$$

The value for ρ, given in Table III, is to be compared with the recent theoretical value of $.209 \times 10^{-8}$ obtained by Bleick and Mayer [11] who investigated theoretically the repulsive potential between two like atoms. Their numerical calculations for two neon atoms show that at a distance of 3.2 Å., which is the lattice constant of solid neon, the repulsive potential is 0.4×10^{-14} ergs. Using the empirical constants found above one finds that the repulsive potential per pair

[10] Jones and Ingham, *P. R. S.* (London), **A-112**, 214 (1926).
[11] Bleick and Mayer, *J. Chem. Phys.*, **2**, 252 (1934).

of neon atoms in the crystal is 0.73×10^{-14} ergs. The greater repulsion in the crystal over that in the gas for a given distance of separation suggests that a more diffuse electron distribution function must be assigned to a neon atom in the crystal state. Presumably the high degree of degeneracy of the energy levels of the solid causes, by some exchange phenomena, this increase in the repulsive energy.

The attraction potential may be expected to be only slightly dependent on the change in state because its origin is in the polarization of one atom by the electric field of the others. The behavior of this potential is classical and should be additively valid for any number of coördinating atoms. At any rate, this is postulated in this article.

Similar considerations for argon yield the following values assembled in Table III.

TABLE III.

	r_0 $\times 10^8$.	α $\times 10^{24}$.	c_{ij} $\times 10^{60}$.	d_{ij} $\times 10^{78}$.	$\Delta H_{\text{Sub.}}$ $\times 10^{12}$.	E_0 $\times 10^{12}$.	ρ $\times 10^8$.	b.
Ne....	3.20	0.39	11.4	11.0	0.293	.098	.276	8.01×10^{-10}
A.....	3.79	1.63	67.4	91.8	1.262	.131	.134	1.27×10^{-2}

THE CRYSTAL VIBRATIONS.

Having obtained the necessary values for the constants, we investigate the dynamics of the small vibrations of a face-centered cubic lattice by the method of Born and Karman.[12]

Consider a wave moving along, say, the X axis of Fig. 1. Then the general equations of motion are given below, together with the corresponding solutions. The reference atom is denoted by the Miller index (l, m, n):

$$m\frac{\partial^2 u_{l,m,n}}{\partial t^2} + X_{l,m,n} = 0, \qquad u_{l,m,n} = ue^{i(\nu t + l\phi + m\psi + n\chi)},$$

$$m\frac{\partial^2 v_{l,m,n}}{\partial t^2} + Y_{l,m,n} = 0, \qquad v_{l,m,n} = ve^{i(\nu t + l\phi + m\psi + n\chi)},$$

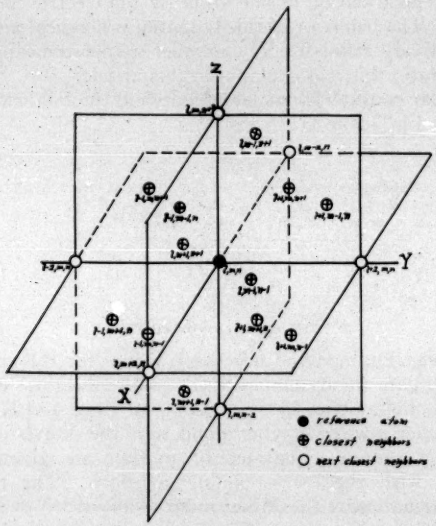
$$m\frac{\partial^2 w_{l,m,n}}{\partial t^2} + Z_{l,m,n} = 0, \qquad w_{l,m,n} = we^{i(\nu t + l\phi + m\psi + n\chi)}.$$

[12] Born, "Atomtheorie der Festem Zustandes."

$u_{l,m,n}$, $v_{l,m,n}$, and $w_{l,m,n}$ are the displacements of the particle at (l, m, n) in the X, Y, Z direction respectively; $X_{l,m,n}$, $Y_{l,m,n}$, $Z_{l,m,n}$ is the force set up in the X, Y, Z direction respectively; finally ϕ, ψ, χ are the "phase-components" of the wave (see Born, l. c.).

We now denote by α, the force constant between the reference atom and the neighboring atoms in the XZ plane;

FIG. 1.



by β the constant between the reference atom and its neighbors in YZ; by γ the constant between the reference atom and its neighbors in XY; by δ the constant between the reference atom and the next closest neighbor in the XZ plane; finally by ϵ that between the reference atom and the four next closest neighbors in the YZ plane. Then the following expression can be derived for $X_{l,m,n}$; expressions for $Y_{l,m,n}$ and $Z_{l,m,n}$ may be written by cyclic permutation of the indices:

$$\begin{aligned} X_{l,m,n} = \alpha(&u_{l+1,m,n+1} + u_{l-1,m,n+1} + u_{l+1,m,n-1} \\ &+ u_{l-1,m,n-1} - 4u_{l,m,n}) \\ + \beta(&u_{l,m+1,n+1} + u_{l,m-1,n+1} + u_{l,m+1,n-1} \\ &+ u_{l,m-1,n-1} - 4u_{l,m,n}) \\ + \gamma(&u_{l+1,m+1,n} + u_{l-1,m+1,n} + u_{l+1,m-1,n} \\ &+ u_{l-1,m-1,n} - 4u_{l,m,n}) \\ + \delta(&u_{l+2,m,n} + u_{l-2,m,n} - 2u_{l,m,n}) \\ + \epsilon(&u_{l,m+2,n} + u_{l,m-2,n} + u_{l,m,n+2} \\ &+ u_{l,m,n-2} - 4u_{l,m,n}). \end{aligned}$$

Substituting the solution into the equation we obtain the secular equation, which can be simplified by the trigonometric relation:

$$\frac{e^{ix} + e^{-ix}}{2} = \cos X.$$

Also, from the definition of ϕ, ψ, χ and from the fact that we are considering a wave moving along the X axis:

$$\phi = \frac{2\pi a}{\lambda} p, \qquad \psi = 0, \qquad \chi = 0$$

wherein (p, q, r) are the cosines of the wave, and $p = 1$, $q = r = 0$; λ is the wave-length and a is the lattice constant. The following two equations for the frequencies are obtained:

$$-m\nu_l^2 = (\alpha + \gamma)\left(4\cos\frac{2\pi a}{\lambda} - 4\right) + \delta\left(2\cos\frac{4\pi a}{\lambda} - 2\right),$$

$$-m\nu_t^2 = (\gamma + \beta)\left(4\cos\frac{2\pi a}{\lambda} - 4\right) + \epsilon\left(2\cos\frac{4\pi a}{\lambda} - 2\right).$$

The ϕ can be written as follows:

$$\frac{\phi}{2} = \frac{\pi a}{\lambda} = \frac{\pi\kappa}{2(N+1)}.$$

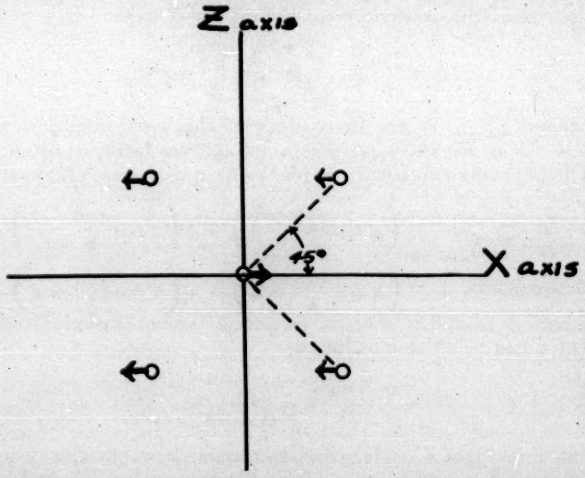
The individual wave-lengths are obtained by allowing κ to take on values up to $N + 1$, where N is the number of particles on an edge of the crystal. Hence the fastest vibration occurs when $\kappa \to N + 1$ or $\phi \cong \pi$ and we have for the frequency in sec.$^{-1}$ instead of (2π) sec.$^{-1}$ the following:

$$\nu_{\max\,(l)} = \frac{1}{\pi}\sqrt{\frac{\alpha+\gamma}{m/2}},$$
$$\nu_{\max\,(t)} = \frac{1}{\pi}\sqrt{\frac{\gamma+\beta}{m/2}}. \qquad (5)$$

Here the frequency denoted by ν_l is identified as the longitudinal frequency because it entails the proper force constants. ν_t is the transverse vibration. It may be seen that the fastest mode of vibration is such that the atoms in some one plane move in the same direction with its immediate neighbors completely out of phase; this also is obtained from the force constants involved.

To evaluate the force constant α, which obviously is equal to γ, we need only consider a single pair of atoms, since the force constants were so defined. Referring to Fig. 2, the

FIG. 2.



force constant for the mode of motion considered is given as follows:

$$\alpha = \frac{\partial^2\Phi}{\partial r^2}\left(\frac{x^2}{r^2}\right) + \left(\frac{1}{r_0}\frac{\partial\Phi}{\partial r}\right)\left(1 - \frac{x^2}{r^2}\right).$$

Here

$$\left(\frac{1}{r_0}\frac{\partial\Phi}{\partial r}\right) = \frac{1}{2}\left[+\frac{6c_{ij}}{r_0^8} + \frac{8d_{ij}}{r_0^{10}} - \frac{b}{r_0\rho}e^{-r_0/\rho}\right],$$

$$\frac{\partial^2\Phi}{\partial r^2} = \frac{1}{2}\left[-\frac{42c_{ij}}{r_0^8} - \frac{72d_{ij}}{r_0^{10}} + \frac{b}{\rho^2}e^{-r_0/\rho}\right].$$

Since $x^2/r_0^2 = \frac{1}{2}$ we obtain by evaluating the first and second derivatives the results in Table IV.

TABLE IV.

	$\frac{r_0}{1}\frac{\partial r}{\partial\Phi}$.	$\frac{\partial^2\Phi}{\partial r^2}$.	$\alpha(=\gamma)$.	$\theta = \frac{h\nu}{k}$.	$\theta_{exp.}$
Ne	-0.007×10^3	$+0.234 \times 10^3$	0.114×10^3	56	63
A	-0.011×10^3	$+1.425 \times 10^3$	0.707×10^3	98	85

The maximum longitudinal frequency which has been calculated is to be identified with the Debye θ_{max}. Any other frequency which might be calculated would be less than this. The agreement between the theoretical θ_{max} and the value calculated from heat capacity data is all that one can expect when the data used is viewed in retrospect.

The author takes this opportunity to thank Professor D. H. Andrews for advice and suggestions.

URBANA, ILLINOIS,
September 20, 1934.

Liquid Coal.—(*Engineering*, Vol. **139**, no. 3603.) Considerable interest is attached to a process devised by MR. S. L. WYNDHAM and demonstrated recently in Cardiff. The coal is first dried so as to reduce its moisture content to about 4 per cent. In a specially constructed machine, oil is sprayed into the coal chamber and mixed with the coal, after which it is formed into a paste. By passing the paste through a series of mills the coal particles are reduced to a fineness such that 99 per cent. passes through a 200 IMM mesh sieve. The plant is said to have an output of 100 tons in a week of 160 hours and to have an electrical consumption of some 20 KWH. per ton. No chemicals are required, no pre-grinding is necessary and there is an absence of by-products. The most suitable proportions for the mixture for general use is 50 per cent. coal and 50 per cent. oil. The coal employed had a gross calorific value of 14,360 B.t.u. per pound and was capable of passing through a 1/8 in. mesh. This coal was mixed with an equal quantity of fuel oil known as Persoleum which has a calorific value of 19,373 B.t.u. per pound, making the value of the resulting product 16,866 B.t.u. per pound. The liquid is stable for a minimum period of four months at normal temperatures. It can be pumped at all temperatures. One ton occupies about 33 cu. ft. Combustion of the coal and oil from a burner takes place almost simultaneously.

R. H. O.

THE VELOCITY OF THE SHOCK WAVE NOT AFFECTED BY THE RATE OF DETONATION OF AN EXPLOSIVE.[1]

BY

D. B. GAWTHROP.[2]

When an explosive is fired from a borehole without the use of stemming it not only emits flame and a considerable volume of gases but also a shock wave which is transmitted to the surrounding atmosphere. This is the concussion effect apparent on the ear to a greater or less degree when the shot is fired.

The shock wave is a discontinuous wave motion advancing in the air ahead of any forward movement of the gases from the explosive. It expands in all directions spherically if in unconfined space, causing a reduction in velocity, and ultimately the wave degenerates into a normal sound wave.

The present investigation was made to determine the velocities of the shock waves sent out by explosives having widely different rates of detonation. Definite indications have been obtained that the rate of detonation is a factor affecting the safety of explosives when fired in the presence of firedamp.[3] It was thought that explosives of high rate of detonation would produce shock waves of higher velocities which would perhaps indicate the mechanism by which the rate of detonation affected the ignition of an inflammable gas mixture.

METHOD OF MEASURING SHOCK WAVE VELOCITIES.

The Schlieren method has been developed to measure the velocities of discontinuous wave motions photographically. The method depends essentially on the refraction of a beam of light at the surface of the shock wave as it advances in undisturbed air. A comprehensive survey of the literature

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[1] Published by permission of the Director, U. S. Bureau of Mines.

[2] Assistant explosives engineer, Bureau of Mines, Pittsburgh Experiment Station.

[3] Perrott, G. St. J., "Factors in the Ignition of Methane and Coal Dust by Explosives," *Min. and Met.*, No. 1604-F, October, 1926, p. 13.

and a description of the apparatus is to be found in a paper by Gawthrop, Shepherd, and Perrott.[4]

Velocity measurements were made from Schlieren photographs taken on a moving film through a slit 0.5 mm. in width. The Schlieren camera covers a field of view 30 cm. in width. A composite photograph, giving a continuous record of the velocity of the shock wave, was obtained from photographs of five successive shots with the camera arranged to photograph five successive 30 cm. distances, starting at the mouth of the borehole.

BRIEF DESCRIPTION OF TESTS.

Charges of explosives equivalent in ballistic strength to 100 grams of Pittsburgh Testing Station 40 per cent. straight dynamite were fired without stemming from a cannon having a borehole 21½ inches in length and 2¼ inches in diameter. Cartridges 1¼ inches in diameter were loaded in the back of the borehole and detonation initiated by no. 6 electric blasting caps located at the back of the charge.

The velocity of the shock wave sent out was recorded for 4 permissible explosives (3 of the ammonium nitrate type and 1 of the gelatin type), and Pittsburgh Testing Station 40 per cent. straight dynamite.

Table 1 includes the physical characteristics, weights of charges fired, and measured average velocities of the shock

TABLE 1.

Physical characteristics and average velocities of the shock wave of explosives tested.

Type.	Sample No.	Density.	Unit Defective Charge.	Equivalent Charges Fired.	Rate of Detonation.	Average Velocity of Shock Wave at Equal Distances from the Mouth of the Borehole, Meters per Second.				
						15 cm.	45 cm.	75 cm.	105 cm.	135 cm.
		g./cc.	gms.	gms.	m/s.					
Permissible 1a	1	0.98	228	100	2610	1670	990	730	560	450
do.....	2	0.95	225	100	3570	1950	1135	730	575	470
do.....	3	0.71	219	98	2670	1695	1000	660	550	475
Permissible 6.	4	1.46	265	116	3300	1770	990	690	540	450
40 per cent. straight....	5	1.42	227	100	4920	1710	1085	675	565	470

[4] Gawthrop, D. B., Sheperd, W. C. F., and Perrott, G. St. J., "Photography of Waves and Vortices Produced by the Discharge of an Explosive," JOUR. OF FRANK. INST., 211, 1931, pp. 67–86.

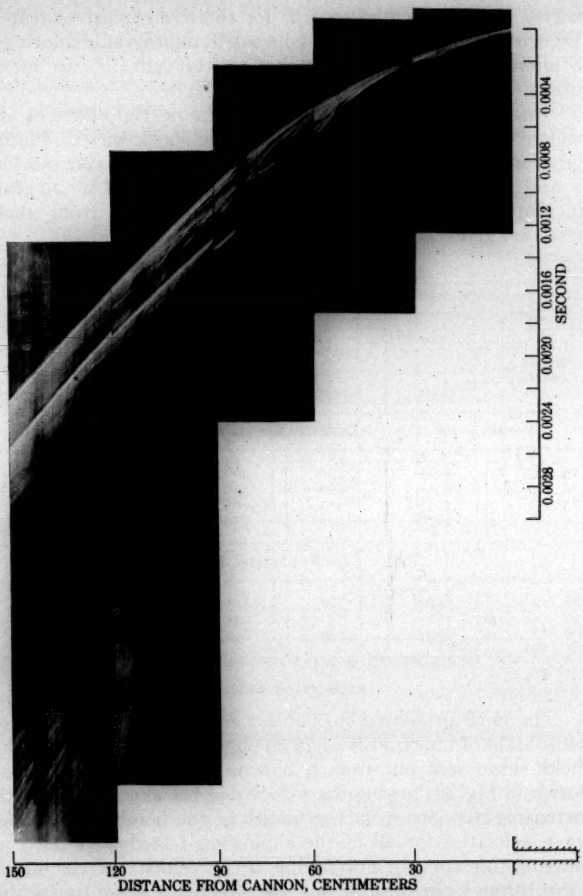

Figure 1.—Photographic record of the shock wave, flame and gases from a blow-out shot.

waves from duplicated records for the five explosives tested. Figure 1 is a representative composite photograph showing a Schlieren record from which shock-wave velocities are measured.

Further tests were made to determine the effect of the weight of charge on the velocity of the shock wave. Photographic records were made when charges of explosive samples 1 and 2 were increased from 25 to 100 grams in 25-gram increments. Velocity measurements obtained from these tests are given in Table 2.

TABLE 2.

Average velocity of shock wave sent out by varying weights of explosive samples 1 and 2.

Weight of Charge, g.	Average Velocity of Shock Wave at Equal Distances from the Mouth of the Borehole, Meters per Second.				
	15 cm.	45 cm.	75 cm.	105 cm.	135 cm.
Explosive Sample 1.					
25	1135	730	480	390	350
50	1355	750	550	450	410
75	1535	915	665	505	420
100	1670	990	730	560	450
Explosive Sample 2.					
25	1180	730	475	410	365
50	1580	830	645	480	410
100	1950	1135	730	575	470

RESULTS OF TESTS.

The data presented in Table 1 indicate that the rate of detonation of an explosive has no effect on the velocity of the shock wave sent out from a blown-out shot. A curve was drawn in Fig. 2 showing the velocity of the shock wave, with increasing distance from the mouth of the borehole. Shock-wave velocities for all of the explosives tested were used in plotting this curve. For sample 2 the velocity of the shock wave through the first 60 cm. was affected apparently by the flame sent out of the borehole.

The velocity of the shock wave increases when the weight of explosive fired is increased. Velocity measurements are

given in Table 2 in which the weight of charge for samples 1 and 2 was increased progressively from 25 to 100 grams. Curves plotted in Fig. 3 show that the increase in velocity of the shock wave with increased charge weight is greatest near the mouth of the borehole. With samples 1 and 2 the average increase in the velocity of the shock wave 15 cm from

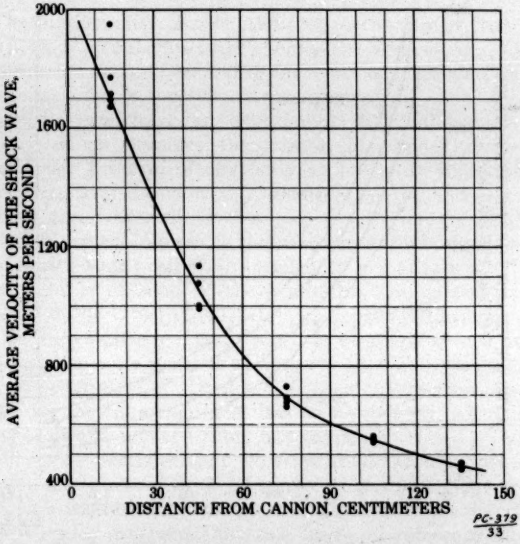

Figure 2 -Average velocity of the shock wave sent out by charges of explosives of equivalent strength

the mouth of the cannon is 650 meters per second, and 102 meters per second at 135 cm. from the mouth of the cannon.

CONCLUSIONS.

Since the velocity of the shock wave sent out by an explosive is not affected by the rate of detonation, only negative evidence can be presented concerning the effect of the rate of detonation on the safety of a shot in the presence

of firedamp. Equivalent charges of explosives such as Permissible Sample 1 and Pittsburgh Testing Station 40 per cent. straight dynamite, send out shock waves of approximately the same velocities which are not comparable to the differences in relative safety and rate of detonation of these explosives.

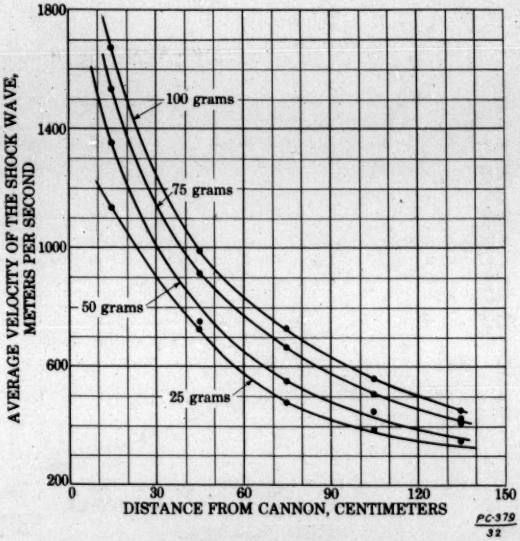

Figure 3 -Average velocity of the shock wave sent out by charges of sample 1

The increase in the velocity of the shock wave with increase in weight of charge of an explosive is comparable to the decrease in safety in firedamp of an explosive as the weight of charge is increased. Shepherd [5] has indicated how the shock wave affects the ignition of firedamp, and it is significant that as the safety of a shot is decreased the velocity of the shock wave increases.

[5] Shepherd, W. C. F., "The Ignition of Firedamp by Explosives," Bull. 354, Bureau of Mines, 1932, pp. 24–26.

MECHANISM.

BY

A. A. MERRILL.

The fundamental characteristic of mechanism is that the repetition of a cause produces exactly the same effect. Only when this is so is prediction possible, since one can not predict a *first* effect; but is repetition ever possible?

Suppose we make an experiment in a laboratory on Monday which involves the motion of some body. We describe the position of the body at the start in terms of space, that is in terms of x, y, z at t_0. At the end of some specified time interval, determined say by the beats of a pendulum, we again observe the position of the body in space and describe that position in terms of x, y, z at t_n where "n" is the number of beats of the pendulum. Suppose that on Tuesday we go into the laboratory to repeat the experiment. We fix the conditions at the start in terms of x, y, z at t_0; we allow the same number of beats to pass and we describe the end in terms of x, y, z at t_n. If then our descriptions are similar we *say* the experiment has been repeated, whereas as a matter of fact no such thing has happened.

When we described our experiment on Monday we had to do so relative to some local frame of reference, namely the particular x, y, z we arbitrarily chose, and when we described it on Tuesday we used the same frame of reference but in doing this do we not tacitly assume that our frame of reference is fixed in space? Surely we have no right to assume this. Obviously our local frame moves with the earth and the solar system and it is only by *neglecting* these motions, and many others that it is possible for us to *create* (not discover) repetition. We are thus faced with the following strange situation. The basis of all prediction in science is an assumption which is not true in fact. Repetition does not exist in the objective world, it is created by us the moment we set up a local frame of reference with which to describe reality. Repetition seems to be true only because we confine our attention to small

local frames of reference and we ignore everything outside of this frame because it does not help our acts. The smaller and more local our frame of reference (point of view) provided we keep it *macroscopic*, the more certain we are that repetition takes place and that prediction is possible. When we jump from the macroscopic to the *microscopic* worlds we find another difficulty regarding repetition and prediction (quanta phenomena) but that does not concern us here. There is of course no fault to be found with our practise of restricting and localizing our frames of reference. We have to do it as an aid to action, but let us be sure that we realize that the conclusions we reach by these methods are only *partial truths*, local with us (relativity); they certainly are not universal truths.

So far I have mentioned only the error of assuming that our frame of reference is at rest absolutely. So long as we deal only with action on this earth, to assume that the earth is fixed in space does no harm. In astronomy of course this error can not be ignored. There is however another error in our method of observing experiments in a laboratory of physics which certainly can not be ignored even on this earth, when considering the living. When we began the experiment on Tuesday we wrote out the equation in terms of x, y, z (space) at t_0. This is also what we did on Monday, but note that our t_0 of Tuesday is twenty-four hours later than our t_0 of Monday. We used exactly the same symbol to represent what were in fact entirely different instants of *time*. We erroneously assumed that *time* stopped from Monday to Tuesday, just as we erroneously assumed that our space frame was at rest absolutely. It is just these two common errors of assuming that *motion* and *time* can be correctly represented by *static* things (lines and numbers) which cause a lot of trouble in modern physics. For instance, it is inevitable that when we try to represent graphically a correlation between something and *time*, we must draw a frame of reference of which one axis is the "t" axis. On this axis we mark two points which we label t_1 and t_2 which points will be separated by a space interval. It is all right for us to do this because we have to do it, but we must be very careful to remember that this picture is a very distorted view of

reality because t_1 and t_2 can not truthfully represent two different instants of *time* since I see them both *simultaneously*. You put them down for the very purpose of showing them to me *simultaneously*, but that very action of yours has turned *time* into space. The "t of physics" is not *time*, and to mix up the "t" of physics with the *time* that we live has caused a lot of trouble, both in physics (relativity) and in biology.

It is certain that to treat *time* as a *static* thing (which is the way we have to treat "t" in mathematical physics) will cause misconceptions in biology. When dealing with living organisms their reactions can be understood only in terms of their history. If we arbitrarily assume a t_0 at the birth of the organism then, as *time* flows on, the subscripts for "t" will be constantly increasing and if we observe two experiments at different times our description should read x, y, z at $t_5 \cdots x$, y, z at t_6 for one experiment and x, y, z at t_{81}, x, y, z, at t_{82} (say) for a later experiment. Only on the assumption that t_0 does not recur and that t_5, t_6, t_{81}, t_{82} occur *only once*, can history have any meaning. This history is what Bergson calls "duration" and Spengler calls "destiny."

Of course all living action is not of this type. There are many acts (habits and tropisms for instance) which can be correctly described at the start by equations in which t_0 enters. This means that mechanism is a good scale for measuring many, perhaps a majority, of living acts. We are machines, yes; but we are also something different and more than a machine because we sometimes show *spontaneity* and by spontaneity I mean that in the description of the spontaneous act you can not introduce t_0, because that would ignore history (personal to the organism) and it is our whole past history that determines the spontaneous act. The spontaneous act is determined, yes; but it is *not* predictable because its "cause" occurs *only once*. That is the vital point. The spontaneous creative artist is farthest away from mechanism and hence the quality of his work is hardest to predict. On the other hand the majority of human beings, as they grow up physically, become more and more like machines, and it is easier and easier to predict their acts.

I think there is a blindness in most of us in that we do not see that we, as conscious human beings, *create* repetition

by choosing a frame of reference which will show it. Francis Bacon (I think) said "If you know what to put in and what to leave out (in your premise) you can prove anything you please quite conclusively." Just so, a blindness to that truth causes trouble in this world. The intellect chooses "what to put in and what to leave out" in order to help us *act*. But in thus choosing a narrow frame of reference (point of view) we forget that we leave out of account all the rest of reality. It is just this process of ignoring most of reality that gives us "mechanism." This narrowness seems to be necessary so far as our contact with the inanimate world is concerned, but I think this narrowness causes much trouble in our social life. We have to choose a frame of reference (standard of value) which suits us; no fault can be found with that at all, but then we make the mistake of thinking that other people should use our frame of reference. That blunder is the basis of all forms of tyranny.

The spontaneous act involves our *whole* personality; probably nothing in our past is negligible for this act. Manifestly therefore in this case there can be no repetition and hence no accurate prediction. Mechanism does not apply here.

If we assume that our space frame is at rest absolutely and if we assume that our "t" (not *time*) is an independent variable, then we are bound to get mechanism. But this intellectual process will fail completely if we try to use it to understand the living except when they are *not* spontaneous. What makes our predictions so uncertain is that we human beings are neither wholly the one nor the other, that is we are not wholly mechanical nor wholly spontaneous, and nobody knows, not even ourselves, when we are going to change. We have only to think of the faculty of *memory* to realize how absurd it is to treat *time* (not "t") as an independent variable or to treat *time* (not "t") and *space* as similar characteristics of one continuum. In mathematics our symbols (t and x, y, z) can represent similar dimensions of a four dimensional geometry, but mathematics deals only with ideas in human brains; it deals with *concepts* never with *percepts*.

There are of course an infinite number of ways in which we can cut up our space frame, because it is only a *concept*, and

one way is just as true as any other way, although there may be a great difference in the value of different ways considered as aids to action. By choosing the proper set of axioms and definitions, we can create any geometry we please, and this choosing *is* just our private way of cutting up a concept into frames that will help us and that is all it is. In a sense, the intellect is only a machine designed to create tools which tools help us enormously when we have to handle inanimate matter. The great difference between humans and the lower animals, is in our ability to use tools suited to the inanimate world, and this ability has been given to us through the intellectual development of our brains.

If scientists feel that they must describe the living with mathematical equations they must never allow themselves to repeat the "t" subscript. Each conscious organism cuts up *time* in its own particular way and this *time* constitutes for it, its own unique history. It is just here that the living transcend mechanism. It is not that we are not machines; we are machines, perhaps most of the time, but we are machines *plus*, and in just the proportion that this *plus* grows in magnitude, in that proportion do we transcend mechanism and take on some of the qualities of the Creator.

For humans, life is, in a sense, a struggle between repetition and creation. Inert matter tries to hold us fast to repetition, but the *life force* (élan vital) within us constantly urges us towards creation; just that is the meaning of growth. In youth this urge dominates us, but as we grow older, inert matter triumphs; we become machines we lose all mental flexibility; we think statically; we become tied to precedent. It is just this conflict between mechanism, the static, and creation, the dynamic, that produces social friction and wars.

The Combustion Turbine. (*Power*, Vol. **79**, no. 2. W. E. TRUMPLER.) The combustion turbine, once deemed economically impracticable, demands new consideration in the light of today's higher turbine and compressor efficiencies and the ability of modern turbine blades to withstand high temperatures. An arrangement is described which promises a satisfactory solution of the combustion turbine. It has to do with a constant pressure cycle with regeneration of the exhaust heat. The compressor is coupled directly to the turbine. Preheater and burner are interposed between compressor and turbine. The driven machine is also coupled to the turbine. Air is compressed in the compressor, heating it slightly, and enters the preheater which heats it nearly to turbine exhaust temperature. From the preheater it enters the burner where fuel is injected and burned with a continuous flame. The fully heated combustion gas enters the turbine, expands through nozzles and wheel, imparting power to the shaft. The partly cooled gas at practically atmospheric pressure leaves the turbine and enters a second passage of the preheater, running counterflow to the first passage. After giving up most of its heat to the compressed air, exhaust leaves the preheater at a slightly higher temperature than that of air at the end of compression. Calculations show that the proposed turbine can compare with steam and oil engine plants. As a possible application it is suggested as particularly adaptable to variable speed drive for centrifugal pump or booster in gas distribution systems.

R. H. O.

SAMPLING ANALYSIS AND SAMPLE SIZE.

BY

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In most sampling experiments the question always arises, "how large a sample is necessary?" It can be shown that the answer to such a question depends not only upon the limits of accuracy desired, but also upon two unsuspected factors; first, the degree of assurance that such a limit will be attained, and second, the inherent homogeneity of the material being sampled. The functional relationship between these four quantities; Sample size, tolerance limits, degree of assurance, and homogeneity, may be derived in the following manner.

Consider a "lot" or aggregate, some characteristic of which has to be determined by sampling experiments. Imagine the entire lot to be made up of a large number of equal sized units or "increments," among which the characteristic is normally distributed with a mean value per increment of $\bar{x}$, and standard deviation σ. Let x be the allowed limit of tolerance (expressed as a decimal fraction of $\bar{x}$) and let y be the desired degree of assurance of not exceeding that tolerance (expressed as a probability, for example, $y = .99$ meaning that there is only one chance in a hundred that the tolerance limits will be exceeded, .999 meaning one chance in a thousand, etc.). It is of course impossible to attain absolute certainty as to a given accuracy unless the entire lot is analyzed. There must of necessity be an element of uncertainty in any determination which is based on sampling processes. A collection of n increments, chosen at random from the entire lot, will, in accordance with existing convention, be referred to as a "sample of size n."

It is required then, that the deviation x on either side of the mean $\bar{x}$ corresponding to a probability y shall be equal to or less than $x\bar{x}$. This may be expressed by the general con-

dition that the quantity whose error function is y shall be equal to or less than $x\bar{x}/\sigma$. The deviation is expressed in terms of σ because such deviations are given in terms of σ in all error function tables. Next, using the operator "erf" to express the error function, that is, $\text{erf}\,(x) = \sqrt{\frac{2}{\pi}}\int_0^x e^{-x^2/2}dx$, the desired condition may be put in the form of an inequality,

$$\text{erf}^{-1}\,(y) \leqq \frac{x\bar{x}}{\sigma}, \tag{1}$$

in which erf^{-1} is an operator signifying the inverse of erf, just as $\sin^{-1}(x)$ is the inverse of $\sin(x)$. The expected values of $\bar{x}$ and σ determined from samples of size n are $\bar{x}$ and $\frac{\sigma}{\sqrt{n}}$ respectively, so that for samples of size n, equation (1) becomes $\text{erf}^{-1}\,(y) \leqq \frac{x\bar{x}\sqrt{n}}{\sigma}$.

Solving,

$$n \geqq \left(\frac{\sigma}{\bar{x}}\right)^2\left(\frac{1}{x}\right)^2\Big[\text{erf}^{-1}\,(y)\Big]^2. \tag{2}$$

But the quantity $\sigma/\bar{x}$ is the well known expression for the coefficient of variability, a number which indicates the inherent variability of the material with respect to the characteristic under consideration. Denoting this coefficient by the symbol S, we have the final relationship

$$n \geqq \frac{S^2}{x^2}[\text{erf}^{-1}\,(y)]^2. \tag{3}$$

As an illustration, suppose a 99 per cent. assurance is required that an error of less than 1 per cent. will be made in the determination of the ash content of a certain lot of coal, and that preliminary tests on one pound increments have shown a variability of 20 per cent. Then equation (3) gives

$$n \geqq \frac{(.20)^2}{(.01)^2}[\text{erf}^{-1}\,(.99)]^2 = 400[2.58]^2 = 2{,}660,$$

thus indicating that a sample consisting of not less than 2,660 randomly chosen, one pound increments, will have to be tested in order to be 99 per cent. certain that the result will be within 1 per cent. of the true value.

The following points are now obvious. First, the size of sample required for a given accuracy, and hence in general the expense, will increase with the square of the heterogeneity of the material. In other words, it is more expensive to test poor material than it is to test good material. Next, the size of sample varies inversely as the square of the tolerance limit x. Thirdly, the size of sample increases rapidly with increase in degree of assurance desired. This may be seen by inspection of the following table.

y	$\text{erf}^{-1}(y)$
.9	1.65
.99	2.58
.999	3.29
.9999	3.89
.99999	4.42
.999999	4.89

Finally, and perhaps most important, since the variability S (usually unknown) appears in the final expression for n, it brings out the unpleasant fact that it is not possible to set a limit to the size of sample required until some information has first been obtained by actual experiment concerning the order of magnitude of the coefficient of variability of the material to be analyzed. Usually, however, past experience with similar materials will indicate an upper limit to S and hence to n.

It is always interesting to compare theoretical predictions with experimental results. In the present case a good opportunity for such a comparison exists in the published experiments of Shewhart (Economic Control of Quality of Manufactured Product, D. Van Nostrand Co. 1931) which give the results of the drawing of 1000 samples from each of three different types of universes, normal, rectangular, and triangular. Taking $S = x$ and $y = .95$, equation (3) shows that n should be equal to or greater than 3.84. Hence, if we take n equal to 4, to correspond with Shewhart's experiments, we should expect the tolerance limits $x\bar{x} = S\bar{x} = \sigma$ to be exceeded at least 45 times out of 1,000 trials. The actual

number of times these limits were exceeded was found to be 48 out of 1,000 for the normal universe, 43 out of 1,000 for the rectangular universe, and 41 out of 1,000 for the triangular universe. This close agreement between theory and experiment is quite striking, both for the case in which the assumption of normality was realized as well as for the two cases of extreme departure from normality. This indicates that the equation gives good results even for cases in which the assumption of normality may not be realized exactly.

NOTES FROM THE U. S. BUREAU OF STANDARDS.*

SPECIFICATIONS FOR FOUNDRY SANDS.

In coöperation with the United States Naval Gun Factory, a study is under way at the Bureau of the various foundry sands which are used in molding practice in the former institution. To date, the physical properties of fourteen types of foundry sands have been studied, and the limits for variation in grain fineness number, grain content class, grain distribution, grain shape, permeability, compressive and tensile strengths, surface hardness, and sintering point have been established. On the basis of these data, purchase specifications have been formulated. Each type of foundry sand requested by bid is required to be equivalent to a reference sample maintained at the National Bureau of Standards upon which physical properties have been determined. Each specification indicates methods for sampling sands and suitable methods of testing are also briefly described. With the uniformity of supplies of sands obtained by these specifications, a standardization of molding practice and general improvement in the castings obtained should be expected.

HARDENING CHARACTERISTICS OF CARBON TOOL STEEL.

Work in progress at the Bureau on the hardening characteristics of 1 per cent. carbon tool steels has clearly demonstrated that the critical quenching rate of a steel of this type may depend not only upon the grain size characteristics of austenite, the high temperature constituent of steel, but also upon the initial structure, existing in the steel before it is heated for quenching and hardening. For example, identical samples of a specific steel which was not a so-called "controlled grain size" steel, were heat treated to produce microstructures which were widely different, coarsely grained lamellar pearlite in one case, and completely sorbitic structure

* Communicated by the Director.

in the second. The pearlitic specimen when quenched in brine from 773° C. (1,425° F.) was more brittle, hardened to a greater depth and had a coarser grained fracture than the companion sorbitic specimen after being quenched from 815° C. (1,500° F.).

It appears possible, therefore, to change a steel from a "deep hardening" to a "shallow hardening" steel, or vice versa, not only by suitably changing the temperature attained just prior to quenching, but also by changing the initial microstructure of the steel. The effect of the initial structure may completely offset the effect of an increase in quenching temperature which might otherwise bring about deeper hardening in the steel.

EXPOSURE TESTS OF SCREEN WIRE-CLOTH.

In 1925, atmospheric exposure tests were started on insect-screen wire-cloth of copper and copper alloys available commercially at that time. The Bureau was requested by the American Society for Testing Materials, sponsor of the investigation, to act as custodian and inspector of the exposed screens and to make such supplementary tests of the materials as might be necessary to interpret the effects of exposure. The Bureau arranged to have the screens exposed on roofs of government buildings at Cristobal, Canal Zone; Portsmouth, Va., Pittsburgh, Pa.; and Washington, D. C. The prevailing atmospheric conditions at these locations may be considered typical of tropical marine, temperate marine, heavy industrial, and mild exposure, respectively.

Similar screens prepared under the supervision of the committee, from each of seven materials, have been exposed continuously to the weather at each of the four locations since 1925. Recently the exposure tests were terminated at all locations except at Washington.

Pending the completion of detailed examinations of the screens and screen materials now in progress and the preparation of the final report, it may be said that copper screen wire-cloth has "held its own" in all locations. Some of the competing materials were found to be very variable in their behavior according to the location.

PREPARATION, USE AND ABUSE OF SPECIFICATIONS FOR PAINT MATERIALS.

In a paper read before the paint symposium of the American Society for Testing Materials, P. H. Walker, chief of the Bureau's paint section, presented his views of what a specification should be and discussed the use of specifications by purchasing agents, including the conditions under which it is unwise to use specifications at all. Mr. Walker also gave a brief account of the development of A. S. T. M. specifications and of government specifications before and after the formation of the Federal Specifications Board, a discussion of the relationship between the Federal Specifications Board's technical committee on paint and Committee D-1 of the A. S. T. M., and a discussion of certain popular misunderstandings as to the functions of the Federal Specifications Board. The kinds of paints and of paint-making materials for which specifications have been prepared by the Federal Specifications Board only, by the A. S. T. M. only, and by both organizations, were listed in four tables. It appears that in general the A. S. T. M. specifies materials used by manufacturers while the Federal Specifications Board covers materials used by the ultimate consumer.

SPECIFICATIONS FOR THE PROTECTION OF UNDERGROUND PIPES.

Within recent years the Bureau has undertaken more than 10,000 field tests of 170 varieties of pipe coatings, and approximately 600 examinations of coatings applied to working lines have been made. These tests, together with those made in the laboratory, have greatly extended the information available on the relative merits of coatings and causes of failure. Nevertheless, data upon which to base a reasonable estimate of whether or not it will pay to apply a coating to a given pipe line are very meager. The use of protective coatings would be advanced by data on the extent to which they reduce the number of leaks, and by the development of specifications which would enable purchasers to call for coatings having definite properties, and under which the delivered material could be tested. Such specifications have not been prepared, but information is available or obtainable

on which adequate specifications could be based. The user of pipe coatings should either develop specifications to cover his requirements or purchase guaranteed protection rather than mere coating materials.

STANDARD TABLES FOR CHROMEL-ALUMEL THERMOCOUPLES.

The most commonly used device for measuring high temperatures is the thermocouple which consists of two wires of dissimilar metals, jointed together at one end (measuring junction). In use the other ends of the wires (reference junctions) are connected to some sensitive electrical indicator. When the measuring junction is at a temperature different from that of the reference junctions an electromotive force is developed which indicates the temperature of the measuring junction when the temperature of the reference junctions is known.

Thermocouples are usually divided into two classes, those made of noble metals (usually metals or alloys of the platinum group), and those made of base metals. Standards have been set up and accepted for noble-metal couples, but very little standardization has been done in the case of base-metal couples which comprise the large majority of all the thermocouples actually used.

As described in the Journal of Research for March (RP767), the pyrometry section of the Bureau has just set up standards for an important type of base-metal couple, namely, chromel versus alumel. A study was made of the characteristics of the chromel-alumel couples now being manufactured, and standard reference tables have been prepared showing the electromotive force for any temperature of the measuring junction, from − 184° to 1,371° C. (− 300° to 2,500° F.) when the reference junction is in melting ice, 0° C. (32° F.). The tables provide the manufacturer of thermocouples with a standard to which his future product can be made to conform, and the user with a criterion for determining whether this product is acceptable. It is also possible by plotting the small deviations of any particular couple from the standard table at a few points to arrive at the deviations at all other points and thus secure a calibration

that is more accurate than could have previously been obtained by this method.

TESTING THERMOCOUPLES AND THERMOCOUPLE MATERIALS.

The application of temperature measurement and control to the innumerable heat treating processes used in the arts and industries, particularly those requiring high temperatures, had hardly started at the beginning of the present century. At present, temperature measurement and control are recognized as indispensable in many processes, and the production of the materials and instruments needed for the purpose has developed into a considerable industry in itself. As described in the preceding item, the thermocouple is one of the simplest, most useful, and most widely employed devices for temperature measurement.

The calibration of a thermocouple consists in determining a table of corresponding values of temperature and voltage. The various methods of calibrating thermocouples and of testing thermocouple materials at the Bureau are described in RP768 in the March number of the *Journal of Research*. The accuracy attainable by the various methods and the precautions necessary in realizing this accuracy are also discussed.

FIRE EXTINGUISHING EQUIPMENT FOR SHIPS.

Twenty years or more ago the Steamboat Inspection Service (now a part of the Bureau of Navigation and Steamboat Inspection) had an approved list of fire extinguishing appliances which were permitted to be used on ships subject to that Service's inspection. It was found that in several instances extinguishers on this list either were not suitable for the type of fire risk for which they were used, or were not constructed so as to give a satisfactory performance. As a result of this situation the Steamboat Inspection Service purchased several samples each of practically every extinguisher which had ever been approved and submitted the entire lot to the Bureau for investigation during 1916 and 1917.

This investigation was made and a report rendered in 1917. The extinguishers were classified into different groups

and it was found that certain whole groups were unsuitable. Other extinguishers, suitable as to type, were found to be improperly constructed or did not give the performance they should. Requirements were set up for those extinguishers which appeared to be suitable. Extinguishers which were found to be unsuitable were then removed from the list of approved extinguishers, and a regulation was adopted by the Steamboat Inspection Service that before any new type of extinguisher could be approved it must first be tested at the Bureau of Standards.

JOINT MEETING OF THE INSTITUTE OF RADIO ENGINEERS AND AMERICAN SECTION, INTERNATIONAL SCIENTIFIC RADIO UNION.

A joint meeting of the Institute of Radio Engineers and the American section of the International Scientific Radio Union will be held in Washington on April 26. There will be two sessions at the National Academy of Sciences Building, 2101 Constitution Avenue, beginning at 10 A.M. and 2 P.M. Papers will be limited to fifteen minutes each to allow time for discussion. The following papers are listed at the time of going to press:

The London general assembly of the International Scientific Radio Union. By J. H. Dellinger, National Bureau of Standards.

Further results of a study of ultra short wave transmission phenomena. By C. R. Englund, A. B. Crawford, and W. W. Mumford, Bell Telephone Laboratories.

Experiments with ultra-high-frequency transmitting antenna in close proximity to the ground. By H. Diamond and F. W. Dunmore, National Bureau of Standards.

Ionosphere measurements during the partial eclipse of the sun of February 3, 1935. By J. P. Schafer and W. M. Goodall, Bell Telephone Laboratories.

The graphical analysis of a 10,000-hour Kennelly-Heaviside layer record. By Harry Rowe Mimno, Harvard University.

Recent ionosphere measurements in the southern hemisphere. By L. V. Berkner, H. W. Wells, and S. L. Seaton, Carnegie Institution of Washington.

Some continued observations of ultra-high-frequency signals over long indirect paths. By Ross A. Hull, American Radio Relay League.

Terrestrial magnetism and its relation to world wide short wave communications. By Henry E. Hallborg, RCA Communications, Inc.

Radio propagation over spherical earth. By C. R. Burrows, Bell Telephone Laboratories.

Direction finding of atmospherics. By John T. Henderson, National Research Council of Canada.

Theoretical explanation of published measurements of vertical plane radiation characteristics of high vertical radiators. By K. A. MacKinnon, Canadian Radio Broadcasting Commission.

Some developments in low loss inductances. By F. E. Terman, Stanford University.

Measurement of high-frequency impedance with networks simulating lines. By W. L. Barrow, Massachusetts Institute of Technology.

The accuracy of the low voltage cathode-ray tube for oscillographic radio measurements. By L. E. Swedlund, Westinghouse Electric and Manufacturing Company.

The detection of frequency modulated waves. By J. G. Chaffee, Bell Telephone Laboratories.

A novel modulation meter. By H. N. Kozanowski, Westinghouse Electric and Manufacturing Company.

On the nature of transmitter key clicks and their suppression. By A. Hoyt Taylor and L. C. Young, U. S. Naval Research Laboratory.

Grid dissipation as a limiting factor in vacuum tube operation. By I. E. Mouromtseff and H. N. Kozanowski, Westinghouse Electric and Manufacturing Company.

Application of secondary emission. By K. V. Zworykin, RCA-Victor Company, Inc.

SUPPLEMENTARY PROGRAM.

(Papers to be presented if time permits.)

A graphical aid in the design of networks for distortion correction. By E. A. Guillemin, Massachusetts Institute of Technology.

The directive antenna of KYW station. By R. N. Harmon, Westinghouse Electric and Manufacturing Company.

Industrial high frequency generators using vacuum tubes. By H. V. Noble, Westinghouse Electric and Manufacturing Company.

THE FRANKLIN INSTITUTE.

STATED MONTHLY MEETING, MARCH 20, 1935.

The regular monthly meeting of The Franklin Institute was called to order at eight-fifteen by the President, Mr. Nathan Hayward.

The President announced that as it was the monthly meeting there would be certain business to be transacted and therefore called upon the Secretary for that business.

The Secretary announced that the minutes of the February meeting had been published in full in the March number of the Journal of the Institute and requested the President to declare the minutes approved as printed if no correction were offered. The President declared the minutes approved as printed.

The Secretary then reported the increase in membership since the last report.

The Secretary reported the appointment of Committees by the President for the ensuing year. The Committees are as follows:

Committee on Library	*Committee on Meetings*
Mr. C. W. Bates	Dr. James Barnes
Dr. H. J. Creighton	Dr. George S. Crampton
Mr. W. G. Ellis	Dr. T. G. Delbridge
Mr. F. Lynwood Garrison	Mr. W. H. Fulweiler
Mr. C. A. Hall	Dr. A. W. Goodspeed
Dr. J. S. Hepburn	Dr. H. McClenahan
Dr. G. A. Hoadley	Mr. Charles Penrose
Mr. L. F. Levy	Dr. G. D. Rosengarten
Dr. Max Trumper	Mr. James G. Vail
Dr. W. T. Taggart	Mr. W. C. Wagner

The following members of the Committee on Science and the Arts were elected to serve for three years:

Mr. Henry Butler Allen	Mr. C. H. Masland, II
Mr. C. W. Bates	Dr. Frederick Palmer, Jr.
Mr. W. L. Brown, 3rd.	Mr. M. M. Price
Mr. E. L. Clark	Mr. J. S. Rogers
Mr. Theobald F. Clark	Mr. Samuel Shoemaker
Dr. T. K. Cleveland	Mr. W. P. Valentine
Dr. T. D. Cope	Mr. F. R. Wadleigh
Mr. W. G. Ellis	Mr. R. L. Wood
Mr. W. H. Kavanaugh	Dr. W. R. Wright
Mr. W. L. LePage	

The Chairman for the present year is Mr. Charles H. Masland, II.

There being no further business, Mr. Hayward introduced the speaker of evening, Dr. Harvey Fletcher of the Bell Telephone Laboratories, Inc. Dr.

Fletcher presented a most interesting paper on the discoveries which he and his collaborators had made concerning the relationships among the intensity, the pitch, the frequency and the quality of musical tones. At the close of his talk Dr. Fletcher was besieged by questions of an informal character by members of the audience. The meeting adjourned at ten o'clock with an expression of appreciation by the President for Dr. Fletcher's delightful talk.

HOWARD MCCLENAHAN,
Secretary.

COMMITTEE ON SCIENCE AND THE ARTS.

(*Abstract of Proceedings of Stated Meeting held Wednesday, March 13, 1935.*)

HALL OF THE COMMITTEE,
PHILADELPHIA, MARCH 13, 1935.

MR. CHARLES H. MASLAND, 2D, *in the Chair.*

The following reports were presented for final action:

No. 2989: Automatic Spooler.

This report recommended the award of Edward Longstreth Medals to Howard D. Colman and Burt A. Peterson, of Rockford, Illinois, "In consideration of the signal advance in the art made by this machine and of the general excellence of its design."

No. 2992: Radio Antenna of the Rhombic Type.

This report recommended the award of the Edward Longstreth Medal to Edmond Bruce, of Red Bank, New Jersey, "In consideration of his design and development of antennæ for short wave communication combining superior efficiency, high directivity, simple construction, and effectiveness over a broad range of frequencies."

No. 3000: Thyrite.

This report recommended the award of the Edward Longstreth Medal to Karl B. McEachron, of Pittsfield, Massachusetts, "In consideration of his careful conduct of a series of closely controlled investigations extending over a period of six years which resulted in the successful development of a process for manufacturing Thyrite."

No. 3001: Clark Medal.

This report recommended the award of the Walton Clark Medal to Frederick Joseph West, of Manchester, England, "In consideration of his outstanding service to the Gas Industry in the sphere of improved scientific development of gas works practice and technique and practical gas research as applied particularly to the carbonization of coal in vertical retorts, and for his work in the training and education of engineers and his success in promoting amicable relationships between employer and employed, all of which have been of substantial value to the Manufactured Gas Industry."

GEO. A. HOADLEY,
Secretary to the Committee.

MEMBERSHIP NOTES.

ELECTIONS TO MEMBERSHIP.

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MR. CARLTON S. FRANCIS, JR., Textile Engineer, Philadelphia, Pa.
MR. HARRY LANGSAM, Patent Attorney, Philadelphia, Pa.
MR. J. H. NOEL, Sales Engineer, Philadelphia, Pa.
MR. GEORGE B. REMMEY, Ceramist, R. C. Remmey Son Company, Philadelphia, Pa.
MR. JOSEPH WINLOCK, Metallurgist, E. G. Budd Company, Philadelphia, Pa. For mailing: 332 W. Springfield Avenue, Chestnut Hill, Phila., Pa.

NON-RESIDENT.

MR. WALTER FLYNN, General Superintendent, of Motive Power and Rolling Stock, New York Central Lines, New York City.
MR. WILLIAM A. HYDE, Director of Research, Leon J. Barrett Company, Worcester, Mass.
MR. ROBERT E. NAUMBERG, New York City.

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NECROLOGY.

Mr. George L. Harrison, Philadelphia, Pa.

LIBRARY NOTES.

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BOOK REVIEWS.

DE LA TURBINE A L'ATOME, by René Bied-Charreton, 198 pages, 13.5 × 21.5 cms. Paris, Gauthier-Villars, 1933. Price 25 francs.

Every so often an engineer attacks some problem of public works with a style that makes the subject very interesting to the layman. There are numerous examples of this miracle of letters scattered through literature. Dr. Beebe is not only a scientist, but he writes with a flare that makes his writings readable without regard to ones serious interest in the marine life off the Bahamas. Many other persons could be cited including René Bied-Charreton.

De la Turbine a l'Atome has its genesis in a wave of electrical engineering. It describes the scramble for water power rights, the slow social control that resulted in order that the "white oil" might be available for the people of France and not damage too seriously the interests of those who had to adjust to this new source of power. From this beginning the book leads to a study of the principles of Carnot, realizations of electric motive power today. There is a chapter on the kinetic theory which is worth reading to repolish general impressions especially to understand how this theory underlies the natural code. The last three chapters are a happy presentation of molecular clusters, radium, the nature (anatomy) of the atom and vibrations. Some of the writing is of a technical interest but much of it will repay the inquiring mind bent on adventure in the French language.

The book opens with a lovely description of evening in the mountains. On page 16:

"L'orage est passé aussi vite qu'il est venu. Laissons-nous tenter par la clarté de la Lune à son plein et escaladons de nouveau la montagne jusqu-aux grandes solitudes qui dominent la vallée. Nous découvrons bientôt le spectacle inoubliable des grands glaciers et des champs de neige éclatants de blancheur et sur lesquels la Lune découpe l'ombre opaque des sommets."

Anyone who has seen the sky in the high mountains broomed to a sparkling clearness by a storm cannot forget the full light of the moon or the profound solitudes or the great glaciers with their flanks of white snow that are made more weird by the black shadows of the mountain peaks where they fall as in the pattern of a quilt, across the whiteness of the snow,—and so on into industrial energy, "white oil," electrical currents that supply power to France.

It's always a pleasure to read a well made book. I have a weakness for French paper backs—I like the economy. Some people hate the insecurity. The binding is important. The well prepared and well typed text inside is of course more important. To end as the book ends:

$$y = \sin x.$$

Domination de l'esprit sur la matiere.

H. W. ELKINTON.

THE ELEMENTS OF THE NEW QUANTUM MECHANICS, by Otto Halpern and Hans Thirring, translated from the German by Henry L. Brose. 215 pages, illustrations, 14.5 × 23 cms. London, Methuen & Co., Ltd. New York, E. P. Dutton & Co., Inc. Price $3.25.

This work originally appeared in two volumes of the well known series "Ergebnisse der Naturwissenschaften" and the authors welcomed the suggestion for its appearance in English translation by Prof. Henry Brose as they felt assured that the work was being placed in experienced hands. It is a record of the changing phases of physical thought during one of the most interesting and fruitful periods in the history of scientific research.

Part I relates the course of development up to 1926. The quantum theory of spectra founded by Bohn in 1913 has impressed its characteristic form on physical research for over fifteen years. Its contradiction with ideas of classical electrodynamics and mechanics was tolerated only on account of the successes of the theory. This position became changed when there were more and more obstacles encountered. The book in this connection gives a good discussion of Bohr's theory and the process of remoulding the theory from its very foundations. In 1925 and 1926 two theories led, in spite of their radically different starting points, to practically the same results. The quantum mechanics founded by Heisenberg is described, as is the wave mechanics of Schrodinger. The account of these theories is intended to meet the need of numerous physicists to grasp the fundamentals.

Part II deals with further developments since 1926. It is an excursion into the realms of the new science developed as a result of the work of Heisenberg and Schrodinger. Extension of general foundations of wave mechanics is treated on as well as the more recent generalization of the theory by Dirac. But before the Dirac theory is discussed a digression on the lines of reasoning and empirical facts of the older quantum theory that lead to the hypothesis of the spinning electron by Uhlenbeck and Goudsmit is interpolated.

A survey is given of the achievements of the theory up to 1929. The subjects include the theory of the Zeeman and Stark effects, the scattering of x-rays, the emission of electrons from cold metals, the photo-electric effect and the relationship of the theory to the statistics of systems of many degrees of freedom (Bose Fermi). The last part discusses the attempts hitherto made to interpret the theory and contains comments on the concepts involved.

The work is a classic which should afford much of value to those concerned with basic physical thought.

R. H. OPPERMANN.

APPLIED ACOUSTICS, by Harry F. Olson, EE., Ph.D., and Frank Massa, B.S., M.Sc., 430 pages, tables, illustrations, 15 × 22 cms. Philadelphia, P. Blakiston's Son & Co., Inc. Price $4.50.

Because the science of acoustics has been brought so much to the forefront in recent years due, among other things, to radio broadcasting and sound motion pictures, a treatment such as this is a very handy and welcome addition to scientific literature. It is more evidence of the development of pure scientific theories to applications for the usefulness of man. When one considers the development of applied acoustics in the last decade, the subject places itself among those which have great possibilities for the future.

The book is a text and reference manual. The basis upon which the general order is followed is (1) the sound source, (2) the transmission of sound through air and its environs, and (3) the sensations produced by the impact of the waves upon the ear drum. As a prerequisite, the reader is assumed to have a knowledge of the general principles of physics, together with a knowledge of the science of communications, particularly the branches concerned with audio frequencies. However, in order that the reader will appreciate the assumptions and implication of the fundamental acoustic equations, these equations are derived before the text proper is taken up.

The text begins with a thorough treatment of dynamical systems, including the derivation of the differential equations from the physical laws and the constants and connections of the system, and the solution of the differential equations. An analogy is drawn between the electrical, mechanical and acoustical systems. The subject of acoustical measurements is fully developed and the present day laboratory technique thoroughly covered.

Aside from the pure theoretical, a considerable part of the book is devoted to practical discussions on microphones, telephone receivers, and loud speakers, their characteristics and behavior under different conditions. Of particular interest should be the authors' contribution on the development of the pressure gradient ribbon microphone. The use of this microphone, due to its novel characteristics, has widened the scope of acoustical measurements and has provided a new and useful tool for the collection of sound in studios and auditoriums.

To make the treatment complete and well rounded there are chapters on architectural acoustics, dealing with reverberation and absorption of sound, physiological acoustics, including response-frequency characteristics of human ears, and miscellaneous acoustic applications. The very good index should prove exceedingly helpful for reference.

R. H. OPPERMANN

EXPERIMENTAL PHYSICS FOR COLLEGES, by Walter A. Schneider, Ph.D., and Lloyd B. Ham, Ph.D. 259 pages, illustrations, tables, 14.5 × 22 cms. New York, The Macmillan Company, 1932. Price $2.25.

As its name implies, this book is intended to be used in conjunction with any general college physics text. Written for the student of elementary physics, it is an admirable treatment not only in the method of presenting the experiments clearly and completely, but of much greater importance, the development of the habit of inquiry and the value of system and order.

Experiments of twenty-three different subjects are described from the simple to the more complex including measurement of the fundamental units of length, mass and time, statics, elasticity, electrolysis and the behavior of light at a plane and curved surface. They are planned so that they illustrate laws which are governed by the same or by a similar set of physical principles. These may be grouped together. At the beginning of each subject treatment there is a discussion of the general theory, followed by directions for each experiment coming under the same subject heading. The purpose of each experiment is very clearly defined.

An outstanding section of the book is Chapter II which discusses the various sources of errors such as personal, accidental, systematic and instrumental, that are liable to creep in during the process of conducting the experiments. It is held that a correct understanding of this makes for order and system.

An index covers experiment headings and subjects to be found in various experiments.

R. H. OPPERMANN.

X-RAYS IN THEORY AND EXPERIMENT, by Arthur H. Compton, Ph.D., Sc.D., LL.D., and Samuel K. Allison, Ph.D. 828 pages, illustrations, 15.5 × 24 cms. New York, D. Van Nostrand Company, Inc. Price $7.50.

Dr. Compton, in the Preface of this book, explains that in his book of 1926 entitled "X-Rays and Electrons" he gave an account of the physics of x-rays as known at that time and that since then there has been a rapid growth of the subject. This necessitated the help of Professor Allison in the preparation of an up-to-date comprehensive discussion of x-rays. That the present volume is a thorough and illuminating treatment can be seen at a glance.

In Chapter I there is a very interesting explanation of the discovery of x-rays, their measurement and absorption, diffraction and spectra. Following this, a treatment on the production of x-rays includes the wave mechanics theory of electromagnetic radiation, L. de Broglie's theory and Schrödinger's theory from which, with the theories of others, a new form of quantum mechanics has been developed. Further, there is covered quite completely the efficiency of x-ray production, the pulse theory and the quantum theories of the continuous spectrum.

Chapter III is devoted to scattered x-rays—interference phenomena, corpuscular aspects, and wave mechanics theory. Chapter IV treats on the dispersion theory applied to x-rays. In this chapter equations are developed similar to those obtained by Lorenz, whose electron theory explains the behavior of the index of refraction in the optical region and gives quantitative agreement with refractive indices for x-rays in regions not too close to the critical absorption

limits. It is shown that this theory predicts an absorption curve for x-rays which is widely different from that experimentally obtained and how, in the effort to remove this discrepancy, a new theory of x-ray dispersion has been developed.

Chapter V presents an account of the methods used in the study of crystal structure and Chapter VI goes more deeply into the subject and investigates such matters as the intensity of reflection, the shape of the intensity versus angle curve near a diffraction maximum, and the resolving power of the diffracting mechanism.

Phenomena associated with the ejection of photo-electrons by x-rays, the interpretation of x-ray spectra, and some accurate methods of x-ray wave-length measurement concludes the text.

Reference is made freely to a large number of books and articles on previous work. This is of great assistance in bringing to mind the subject matter as well as furnishing opportunity for further study. Needless to say, this book gives a comprehensive view of the whole field and is undoubtedly a work of outstanding value.

R. H. OPPERMANN.

ANALYTICAL MECHANICS FOR STUDENTS OF PHYSICS AND ENGINEERING, by H. M. Dadourian, M.A., Ph.D. 427 pages, illustrations, 15 × 23 cms. New York, D. Van Nostrand Company, 1931. Price $4.00.

The third edition of a remarkable text in which many pages have been rewritten resulting in improvement of presentation, and in which new material has been added. For the purpose of equipping the reader with an essential tool, Chapter I explains the addition and resolution of vectors. The subject thereafter may be divided into two parts—(1) Statics, or the mechanics of bodies in equilibrium, and (2) kinetics, or the mechanics of bodies in motion.

In the first part (statics) bodies in equilibrium, namely particles, rigid bodies, framed structures and flexible cords are treated. The subject of graphic statics is introduced in connection with framed structures. The second part is given to discussions of problems in kinetics. These include subjects such as work, energy, fields of force, momentum, and periodic motion.

Two useful conceptions known as center of mass and moment of inertia, which greatly simplify discussions of the motion of rigid bodies are dealt with in a separate chapter. The Calculus is applied here. Velocity and acceleration are also treated in a separate chapter.

The problems at the end of each chapter appear to have been designed so that their solution requires a thorough knowledge of the subject and to make them as practical as possible.

Written with the aim to present the subject in such a manner as to enable the student to acquire a firm grasp of the fundamental principles and to apply them to problems with a minimum amount of mental effort, this book is an excellent text for use as a foundation for the study of engineering.

R. H. OPPERMANN.

THE ELECTRONIC STRUCTURE AND PROPERTIES OF MATTER, AN INTRODUCTORY STUDY OF CERTAIN PROPERTIES OF MATTER IN THE LIGHT OF ATOMIC NUMBERS, BEING VOLUME I OF A COMPREHENSIVE TREATISE OF ATOMIC AND MOLECULAR STRUCTURE, by C. H. Douglas Clark, M.Sc. 374 pages, tables, illustrations, 14 × 22 cms. New York, John Wiley and Sons, Inc. 1934. Price $5.50.

This book is a treatment on the basic theories of physics. Developments in numerous fields have independently from time to time indicated that prevailing theories did not suit all cases and it has seemed necessary to strengthen these theories at an increasing rate in recent years due to accelerated developments. As a result, the research worker in a specialized branch has experienced a need of a method to enable him to view the situation along various avenues of approach. The book is Volume I of a three volume work at present projected. It is stated in the Preface of this book, that the work will be contained in separate volumes, bearing individual titles, each volume being as far as possible complete in itself as an expression of some leading thought.

The present volume is divided into two parts. In Part I General Introduction there is contained five Chapters discussing classification of the elements and of atomic electrons, optical and x-ray spectra, the transitional and rare earth elements, and valency and chemical combination. In Part II, the larger portion of the book, the bearing of physical behavior upon molecular constitution is introduced. Under the heading of "Melting Points and Boiling Points" there is first dealt with the polar, then the homopolar compounds and lastly certain general conclusions that have been reached. The treatment on atomic and molecular volumes is conveniently followed by that of atomic and ionic radii.

A very well set up Chapter and very interesting one is that devoted to electrical conductivity. Apart from insulators and dielectric media, substances are classified into three groups in respect to electrical conductivity. They are metallic conductors, ionic conductors, and half conductors. Each of these is discussed in a very clear manner. Electrical conductivity of crystals, of melted compounds, and conductivity and temperature, should prove illuminating and refreshing to a great many readers.

Similarly, following chapters on magnetism cohesional properties, and entropy reveal much of interest and value in bringing the subject matter up to date.

Throughout this Volume I of the work, references are made freely and the titles of these are given in full. This occupies considerable space which however is well spent for it facilitates their location. The treatment itself is non-mathematical as far as possible and is a masterful attempt to summarize the explanations which have been advanced in connection with certain properties of matter in terms of electronic constitution.

H. R. OPPERMANN.

THE EARLY YEARS OF MODERN CIVIL ENGINEERING, by Richard Shelton Kirby and Philip Gustave Laurson. 324 pages, plates 16 × 24 cms. New Haven, Yale University Press, 1932. Price $4.00.

What we now call civil engineering was practiced as an art thousands of years ago and evidences of this that we see today indicate that it was practiced with skill and success. It was only in the comparatively recent past, in the seven-

teenth and eighteenth centuries, that mathematics as a tool was taking such shape that it could be readily used in practical calculation. In the art of surveying, for instance, the principles have been understood from time immemorial but it wasn't until this latter period that the methods practiced by the surveyor and the instruments which he used began to resemble those of today. Thus, this book differentiates between the modern and the ancient practice. As its title shows, it deals with the modern profession, its period of early development.

Each of the eleven chapters is devoted to a part of the subject as a whole. The first nine have to do with such parts as canals, bridges, tunnels and subways, waterworks, and river and harbor improvements. A chapter treating on materials is included in which there are narrations on lime and cement research, natural and portland cement, concrete, and other materials. A list of biographical outlines of important men during the development period is given. The book is profusely illustrated and contains listings of a vast number of references.

Because of the masterly make up of this book, its method of presentation, it is interesting and instructive reading to the layman having only a little background of civil engineering knowledge or interest, as well as to the professional man. Incidentally, many members of the profession undoubtedly know little of its history. Aside from being instructive reading, this book should prove invaluable as a reference work. From it directly or from the references listed it is possible to gather sufficient information for a series of lectures on any of the subjects treated. This, however, is only one illustration of how it may be used.

The Early Years of Modern Civil Engineering can be recommended to all who realize the need of an instrument to make life more enjoyable by greater appreciation of the wonders about us.

R. H. OPPERMANN.

THE KINETIC THEORY OF GASES, By Leonard B. Loeb, Professor of Physics, University of California. 687 pages, figures, 15 × 23 cms. New York, McGraw-Hill Book Company, Inc., 1934. Price $6.00.

The thought that "of making many books there is no end" dates back at least to the time of Solomon. But let us hope that there shall be no interruption to the output of the relatively few essentially valuable works such as that under consideration.

Unfortunately the reviewer's graduate studies came to a close too soon to have benifited even from the first edition (1927). Few monographs dealing with such a complex subject have been better conceived and executed from the student's point of view. Preëminent among the virtues are two: (1) a unity of purpose and organization throughout, and (2) a logical and natural development of the material, embracing first a sufficient statement of the problem, then an elementary treatment, largely non-mathematical, followed then successively by closer examination of the assumptions with suitable mathematical redevelopment, and finally by presentation of the latest advances.

Naturally the Kinetic Theory involves the extended use of mathematics. Such developments are given with guiding words from step to step. When the going becomes unreasonably difficult the author (be he commended) calls a spade by its right name and skips the obstacle with suitable references. Thus while paper and ink are freely used, time and patience are much conserved in arriving at

a clear picture of things known and unknown. Any student can quickly find his level and make consistent progress therefrom.

These remarks may apply equally to the first edition. The second edition now takes suitable notice of the change in viewpoint which physics has undergone under the influences of the new era of wave and quantum mechanics (since 1925). At least one-third of the book has been rewritten. The major changes have come in those sections devoted to molecular structure and its influence on molecular behavior. Nearly the whole of the chapter on specific heats has been rewritten. The chapter on viscosity, heat conduction and diffusion has been modernized through introduction of the effects of molecular force fields in place of the older solid elastic impacts. New work on molecular beams is presented and additions and revisions have been made at other places too numerous to mention.

It may be of interest to point out that many important mathematical deductions are to be found developed completely from the basic assumptions. Such are the Boltzmann and the Maxwell developments of the distribution laws and Poisseuille's law of the flow of gases through capillary tubes. Some of the single sections are very long, fourteen pages and upward. Very few errors have been found but attention may be called to the rather confusing omission of negative signs in the equations on page 18, lines 15 and 16. Valuable appendices give data on diameters of molecules, Birge's table of fundamental physical constants, molecular velocities and free paths and values of certain mathematical functions.

LESLIE R. BACON.

THE STORY OF ENERGY, by Morton Mott-Smith, Ph.D., 305 pages, illustrations, 13 × 19 cms. New York, D. Appleton-Century Company, Inc., 1934. Price $2.00.

In this little book, the author has traced the story of man's conquest of energy, described the scientific discoveries that made it possible and explained the chief ways in which energy is applied to useful purposes. Written in the nature of a narrative, it starts with the earliest quest for power, proceeds on through the development of the steam engine, the utilization of heat and heat theories up to a very clear treatment of entropy, mechanical refrigeration and the internal combustion engine.

Very little mathematics is used anywhere in the book even in the chapter on entropy, in fact this together with the charming style of writing make it outstanding. One of the great needs of the times is a means of satisfactory translation from the technical to the everyday. When this is completed there is opened to the layman a method of instructive entertainment which has untold possibilities. This book can here be rightly classed. It is educational and easy to read.

R. H. OPPERMANN.

ELECTROMAGNETISM, by Hector Munro Macdonald, M.A., F.R.S. 178 pages, 14 × 22 cms. London, G. Bell and Sons, Ltd. 1934. Price 12/6.

In the Preface the author states that the object of this book is the development from the fundamental laws of electromagnetism of a consistent scheme for the representation of electrical phenomena, and the derivation of the more immediate consequences of the fundamental laws. In doing this, selection is made of particular problems to be treated in detail and they are chosen because

of their suitability as illustrations of a general method. A knowledge of the elementary Ampere-Faraday properties of electric currents in circuits is assumed.

It begins with a treatment of Ampere's law which gives the relation between electric current and magnetic force, Faraday's law which gives the relation between electric force and the time rate of change of magnetic force, and Fresnel's law of transversality which determines the mode of propagation of electrical effects in free space. It is shown in the analogue of Green's theorem in the theory of potential that the electric and magnetic forces at points outside a closed surface due to a distribution inside the surface can be expressed in terms of the electric and magnetic forces tangential to the surface.

In treating on phenomena which depend on the nature of material media, the material medium can be represented by an electric current distribution and a magnetic current distribution throughout the space where there is matter. There is discussed a number of very important subjects in this connection including the total electric current and magnetic induction at a point, the electric force acting on an electric charge which is in motion, and the relations between electric current and electric force, and between magnetic induction and magnetic force in an isotropic transparent medium.

From here the trend is directed to applications to transparent material media and to conducting media, diffraction, radiation, resonance, and moving electric systems. To review each of these would require much more space than is here allotted.

The very nature of the book is necessarily intensely mathematical. It is a classic and will be much appreciated by those so equipped and by those whose interests lie in the direction of the theories of the subject.

R. H. OPPERMANN.

NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS.

Report No. 495, A Description and Test Results of a Spark-Ignition and a Compression-Ignition 2-Stroke-Cycle Engine, by J. A. Spanogle and E. G. Whitney, 19 pages, illustrations, tables, 23 × 29 cms. Washington, Superintendent of Documents, 1934. Price ten cents.

A single-cylinder, gasoline-injection, spark-ignition, 2-stroke-cycle engine was constructed using a modified air-cooled Liberty engine cylinder and a universal test engine base. The combustion and scavenging air were admitted through piston-controlled ports near the bottom of the cylinder and the exhaust gases discharged through two poppet valves in the cylinder head. The displacement of the engine was 118 cubic inches. Optimum performance was obtained with the inlet air directed into the cylinder at an angle of 20° to the radial. A maximum net brake mean effective pressure of 132 pounds per square inch was obtained at an engine speed of 1,000 r.p.m. A maximum of 43.0 net brake horsepower was obtained at 1,225 r.p.m. The cylinder could not be cooled satisfactorily at high power outputs with an air velocity of 120 miles per hour.

A water-cooled cylinder of the same displacement was constructed to continue the 2-stroke-cycle investigation to higher speeds and under more favorable cooling conditions. Four masked poppet valves in the cylinder head were used for exhaust. The engine could be operated with either spark ignition or compression ignition. With spark ignition a maximum of 69.0 gross brake horsepower

(uncorrected for blower power) was developed at 1,800 r.p.m. using a scavenging pressure of 8.4 inches of mercury—a specific output of 0.585 gross brake horsepower per cubic inch of piston displacement.

More extensive tests were conducted with the engine operating on compression ignition. Inertia of the scavenging air and length of the exhaust pipes had a marked effect on the engine performance. With other conditions constant, the increase in gross power output was found to be proportional to the increase in scavenging pressure.

Report No. 505, Tests of Nacelle-Propeller Combinations in Various Positions with Reference to Wings. IV-Thick Wing—Various Radial-Engine Cowlings—Tandem Propellers, by James G. McHugh. 43 pages, illustrations, tables, 23 × 29 cms. Washington, Superintendent of Documents, 1934. Price fifteen cents.

This report is the fourth of a series giving the results obtained from tests in the N.A.C.A. 20-foot wind tunnel to determine the interference lift and drag and the propulsive efficiency of wing-nacelle-propeller combinations. Previous reports give the results of tests with tractor propellers with various forms of nacelles and engine cowlings. This report gives the results of tests of tandem arrangements of engines and propellers in 11 positions with reference to a thick wing.

The results indicate that with a tandem arrangement of engines and propellers the best over-all efficiency is obtained by using a nacelle of the lowest drag it is possible to obtain without impairing the cooling of the cylinders. Of the several engine-cowling combinations tested, best results were obtained with an N.A.C.A. hood over the front cylinders and a ring over the rear cylinders. When a large nacelle is used with this cowling combination there is little difference between the net efficiencies for positions with the nacelle faired into the wing and positions with the thrust line about half a propeller diameter below the lower surface of the wing, both positions being greatly superior to any position tested above the wing. These positions and cowlings, however, are considerably inferior to the best tractor-propeller arrangements previously reported.

AN INTRODUCTION TO STRUCTURAL THEORY AND DESIGN THEORY, by Hale Sutherland, A.B., S.B., and Harry Lake Bowman, S.M. 318 pages, illustrations, tables, 15 × 23 cms. New York, John Wiley & Sons, Inc. London: Chapman & Hall, Ltd., 1935. Price $3.50.

The second edition of a book introducing the reader to the basic conceptions and principles of structural theory relating to trusses, rigid frames and space frameworks. The arrangement is that of a text book for a 2 or 3 semester course but the practicing engineer will find the material in a convenient form for ready review.

Being merely an introduction, the principles of mechanics are considered in their application to the design of structures. Only the load carrying function of structures is here treated, the dimensioning and preparation of plans for construction is dealt with in another volume. A chapter is included on graphic statics, touching only briefly on elementary concepts as it is assumed that these are fairly well understood. Roof and bridge trusses are next taken up followed by a good

treatment on slope and deflection calculations. It is in this latter treatment that the Bar Chain Method of Elastic Weights for the easier computation of truss deflections is explained. In the chapter on rigid frames, the section devoted to moment distribution presents the method of Professor Hardy Cross which may be applied very quickly and simply for an approximate solution or with a little more labor extended to any degree of exactness desired.

Resistance to horizontal loads of tall buildings due to wind is presented with clarity including solution by the cantilever method, and the portal method. Farther on in the book under the subject of secondary stresses the Cross Method of solution is illustrated.

It is stated that for purposes of illustration free use has been made of structures which differ, often radically from any in actual use. This is done because of the desire to simplify arithmetical labor and so facilitate focusing attention on the principle under discussion, and the wish to compel the thoughtful application of a principle in place of a possible memory solution based on a previous example.

The book is remarkable for its clarity and detail. It is an exceptional illustration of a modern text and it should be valuable to graduated practicing engineers of five or more years out of college not only for the new material presented but for the modern way of presenting this material.

R. H. OPPERMANN.

PUBLICATIONS RECEIVED.

Theory of Alternating Current Wave-Forms, by Philip Kemp. 218 pages, illustrations, tables, 14 × 22.5 cms. Pittsburgh, Instruments Publishing Company, 1935. Price $4.50

Principles of Phase Diagrams, by J. S. Marsh, with a foreword by John Johnston. 193 pages, illustrations, 15.5 × 23.5 cms. New York and London, McGraw-Hill Book Company, Inc., 1935. Price $3.00.

Automatic Protection of A.C. Circuits, by G. W. Stubbings, 293 pages, illustrations, 14 × 22 cms. Pittsburgh, Instruments Publishing Company, 1935. Price $5.00.

Introduction to Electric Transients, by Edwin B. Kurtz and George F. Corcoran. 335 pages, illustrations, tables, 15 × 23.5 cms. New York, John Wiley & Sons, Inc. London, Chapman & Hall, Ltd., 1935. Price $4.50.

United States Coast and Geodetic Survey, Special Publication No. 186. Triangulation in Missouri (1927 Datum) by Walter F. Reynolds. 158 pages, maps, tables, 15 × 23.5 cms. Washington, Government Printing Office, 1934. Price twenty cents (paper cover).

Canada Dominion Bureau of Statistics, Preliminary Report on the Mineral Production of Canada, during the Calendar Year 1934. 42 pages, tables, 16.5 × 24.5 cms. Ottawa, King's Printer, 1935. Report on the Men's Factory Clothing Industry and Clothing Contractors in Canada, 1933. 26 pages, tables, 21.5 × 28 cms. Ottawa, King's Printer, 1935. Report on the Printing Trades in Canada, 1933. 17 pages, tables, 21.5 × 28 cms. Ottawa, King's Printer, 1935.

Bell Telephone Laboratories. Monographs: B-721, The Role of Statistical Method in Economic Standardization, by W. A. Shewhart, 13 pages, illustrations.

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CURRENT TOPICS.

Electric Furnaces for City Gas Production.—(*Gas Age Record*, Vol. 75, No. 6.) M. Böhm described to the Second International Gas Congress at Zurich a distillation furnace for testing purposes at the plant of the Brown-Boveri Corp. at Baden, Switzerland. It was equipped with a drum, a condenser and a recording gage. The furnace proper was a cylindrical iron tube 31½ in. in diameter and 6.56 ft. high with vertical axis. It was insulated inside and out and the ends were sealed with metal discs. A small opening was drilled through the center of each disc through which the cylindrical shaped graphite electrode (4.33 in. in diameter) was inserted until it came in contact with the ignition electrode placed along the axis of the retort. The gas was passed through the drum located at the retort outlet before entering the condenser from which it was passed to the gage and next to a burner. The ignition electrode contained coke in a paper cylinder and around it was the bituminous coal to be carbonized. The retort had a capacity of 600–700 lbs. of coal. Results showed that gas of 569 B.t.u. was produced and that there was 600 cu. ft. (60° F., 30 in. Hg, saturated) per 100 lbs. of coal. Energy absorbed per 100 lbs. of coal was 35.5 kw.hr. In tests at the Reggio-Emilia gas plant a striking improvement resulted from the adoption of a new type ignition electrode. Another improvement permitted the generation of water gas directly during the final phase of the carbonization operation. This resulted in a mixed gas of 472–484 B.t.u. (68 per cent. coal and 32 per cent. water gas). Advantages of the electric carbonization include: (1) Off peak electric energy can be used; (2) First cost of equipment is low; (3) Operation possible to start with retort at working heat, allowing intermittent operation, saving electric energy otherwise expended for preheating. The use of electric heat for making city gas deserves serious study.

R. H. O.

Carbolic Acid in Tank Cars.—Carbolic acid, classified by chemists as "phenol," was best known for its antiseptic and disinfecting value. In the pre-war days, when the virtues of iodine, mercurochrome and the like were yet undisclosed, almost every household had in its medicine cabinet a dilute solution of phenol. The label on the bottle bore usually a bright red skull and cross-bones and the legend: Carbolic Acid—Poison.

It is true, organic chemists early realized the worth of phenol as an intermediate in the preparation of picric acid, hydroquinone, a number of dyes and pharmaceuticals but for the layman no special application was recognized until the advent of artificial plastics involving the well-known phenol-formaldehyde reaction. Now, instead of coming in little bottles, phenol is being shipped in tank cars. The News Edition of the *Ind. & Eng. Chem.*, Vol. 13, No. 4, publishes a photograph of a nickel-clad steel tank car equipped with pure nickel heating coils. The nickel surface protects the phenol against harmful discoloration which is of the utmost importance in the production of plastics of quality.

C.

Improved Enameling Process.—Even if the housewife doesn't care how her enameled kitchen ware is made so long as it looks nice, the manufacturer is always ready to adopt new methods that may involve economies and improvements in his products. The Mellon Institute of Industrial Research has recently announced the development in its laboratories of a new enameling process that achieves a greater degree of opacity, and therefore depth of color, in two coatings than are possible with three in present processes.

The problem in enameling is to secure a firm bond between the under or "ground" coat and the steel. This is accomplished by the addition of chemicals which act similarly to a flux in the welding of metals. Under present methods this "ground" coat is either black or very dark blue. With the new process, called Hommelaya, a white or a light color can be secured in the "ground" coat, and therefore only one additional coating and firing is needed to secure a true color tone.

C.

Advances in Horticulture.—The Bureau of Plant Industry report for the fiscal year ending June 30, 1934, calls attention to encouraging progress in the breeding of crop plants to increase resistance to diseases, and to meet ever-changing demands of the consumer. Several new varieties of wheat, developed for disease resistance, superior quality and high yield were made available to farmers in the last year. Working with the Iowa Agricultural Experiment Station the Bureau has developed four strains of hybrid corn that have consistently outyielded other varieties. New varieties of rice produced in coöperation with the Louisiana Station bring a premium of 30 to 35 cents a barrel over standard commercial varieties.

Two new strains of lettuce of the Iceberg type and one new melon

of the Honey Dew type were introduced last year. In both cases the new strains are practically immune to costly diseases prevalent in Southern California and nearby producing sections. Many treatments—including sprays of almost every description—have been tried for combating downy mildew. So far, the only method that has consistently held the disease in check is heating the soil in the plant bed at night to a temperature of 70 degrees or higher.

Experiments in West Virginia showed that increases up to 630 per cent. in animal gains resulted from the use of fertilizers in building up poor pastures. As the soil fertility of a pasture is increased, better grasses and legumes tend to "come back" and drive out some of the poor grasses and weeds. This helps to explain the large gains from fertilization.

Investigation of the "alkali disease" of live stock, which occurs in certain areas of the northern Great Plains, revealed that selenium compounds absorbed by plants from the soil are responsible. This absorption of selenium depends not so much on the absolute amount of selenium in the soil as on the relative amount with reference to sulfur. Experiments showed that where there is only one part of selenium for every eight parts of sulfur, injury to the plant occurs, but where there are twelve or more parts of sulfur for every part of selenium, the plants are normal.

It also was discovered that lettuce seed regarded as dormant would germinate readily if soaked in water and exposed to a few seconds of sunlight. Later work showed that light rays at the red end of the spectrum were responsible for waking the drowsy seeds.

C.

Treatment of Bursitis.—The use of electricity in the treatment of ills of the human body has much fascination for most of us because both electricity and the human body are what might be called "spectacularly mysterious." The accomplishments are spectacular and the hows and whys are mysterious. The merging together of two or more scientific lines of thought has often resulted in great benefits to man. A very interesting account of the treatment of calcareous deposits just over the sharp angle of the shoulder, between the muscles, is given by Dr. W. R. Whitney in the *General Electric Review* for February, 1935. Using two thyratron tubes arranged to oscillate at about 12,000,000 cycles, a new apparatus was constructed to yield up to 160 watts. To this generator a coil 12 ft. in length was connected and arranged so that it might be coiled about the body or a limb and also used as a flat pad for irregular surfaces. It could therefore be placed in the vicinity of the shoulder and there could

be induced high frequency current of an amount so that a thermometer under the arm would register 105° F., an artificial fever, so to speak.

Shoulder bursitis can often be traced to some harmful local exertion. A painful "stiff" shoulder results and the arm may become almost completely useless. An X-ray may disclose a lime deposit near the bone. Until a few years ago it was best practice to remove the deposit surgically. It now looks as though operation for bursitis might seldom, or never, be necessary. One case of bursitis studied was that of a man who had indulged in more physical exercise than usual. Treatments with the high frequency apparatus eliminated the pain and the deposits as shown by the X-ray. Another case was that of a woman who had had a troublesome shoulder for ten or more years. This was also eliminated. Dr. Whitney points out that while heat application has been employed successfully in such cases by various means, it does not necessarily follow that the action is simply one of dissolution of solids brought about by the warmer plasma. Other very interesting questions are discussed by Dr. Whitney from the point of view of research such as deposits in the arteries and the suggestion of a possible reaction to reduced temperature.

R. H. O.

Sweden Builds a Pumped-Storage Plant.—(*Power*, Vol. 79, no. 3) GEORGE WILLOCK, engineer at Trollhättan, Sweden, describes the plant at Sillre on the Indal River, 40 miles up from the Gulf of Bothonia. The plant operates in combination with Norrfors hydro-electric system of 22,000 kw. capacity on the Umea River, 150 miles north of Sillre. A reservoir cannot be created at Norrfors, so surplus power during off peak periods is transmitted to Sillre to pump water to a storage reservoir 640 ft. above river level, whereby an additional 5,000,000 kw.h. is obtained for peak service. This reservoir has a useful storage capacity of 706,000,000 cu. ft.

Water is brought to the power house through an unlined tunnel 7,500 ft. long and of 176.6 sq. ft. cross section and a penstock 3,051 ft. long by 6 ft. diameter. The power house is designed for three units, but only one, rated at 6000 kw. has been installed.

The pump is a two stage centrifugal type with a capacity of 30,000 to 45,000 g.p.m. against a head of 745 to 600 ft. at a speed of 600 R.P.M. The turbine will develop 10,080 hp. under a maximum head of 656 ft. The 3-phase alternator rated at 50 cycles has a direct coupled exciter. When operating as a motor its output is 7000 kw. at unity power factor. All are connected on one vertical shaft.

Pump test results showed a maximum efficiency of 86 per cent. with discharge of 41,200 g.p.m. against 656 ft. head. A maximum water wheel efficiency of 91.6 per cent. was obtained at about 0.9 rated load and 554 ft. head.

R. H. O.

Stationary Commutator D. C. Motor.—In a paper by Dr. E. F. W. ALEXANDERSON AND A. H. MITAGG presented at the A. I. E. E. winter convention there was announced the development of the Thyratron motor which has series direct current characteristics and operates on alternating current. It was made possible by recent advances in electron tube applications. One such motor is now on test. It is rated at 400 hp. 625 r.p.m., and 75 hp. at 350 r.p.m., and is intended for driving an induced draft fan. The motor speed may be controlled down to a standstill. It operates from 2300 v., 3-phase, 60-cycle power and has a stationary armature and revolving field. The electron tubes perform commutation and grid-controlled rectification, the latter providing continuous power control from standstill to maximum speed.

R. H. O.

A New Source of "Kilocycle Kilowatts."—L. D. MILES, in an article in *Electrical Engineering* for March 1935, explains how electric power at frequencies of 1,000 to 100,000 cycles per second is obtained at low cost by means of an electronic tube known as the arc tube. The arc tube consists essentially of two electrodes closely spaced in inert gas under high pressure. A general-purpose circuit consists of a choke coil, a stabilizing resistor, a capacitator and an inductor in series. The tube is connected across the capacitator and the inductor, and the output at any desired voltage may be taken from the secondary of a transformer which constitutes the inductor. In high power applications the stabilizing resistor may take the form of the ohmic resistance of the windings of an electromagnetic field. The cycle of operation is as follows. When voltage is applied, the capacitator is charged through the resistor, the choke causing a momentary pause in the starting cycle. When the capacitator is charged to the breakdown voltage between the tube electrodes, the tube ionizes, acts as an instantaneous short circuit, and allows the capacitator to discharge through the inductor-capacitator-tube circuit. Line current inrush is prevented by the choke. At the instant the capacitator is completely discharged, a high current is flowing in the inductor-capacitator-tube circuit. The inductor continues current flow, which overdischarges the capacitator and drives the tube voltage negative, whereupon the arc extinguishes

and the tube is again an open circuit. The capacitator again becomes charged and the cycle is repeated. The circuit arrangement however depends upon the type of load, the wave shape and the frequency desired.

The arc tube is destined to supply cheaper power for industrial utilization because it is adaptable to varying needs, the equipment can be made economically to supply a few watts or to furnish 50 or more kilowatts and the operating and maintenance costs are low. There are many present uses of high frequency power in industry as well as new applications that have been awaiting the availability of cheaper kilocycle power.

R. H. O.

Hot-Air Balloons Again In Vogue.—(*Science Service.*) According to the German science weekly, *Die Umschau*, hot-air balloons may soon join gliders as popular sports air-vehicles in that country. A Vienna-born aircraftsman, Rudolf Brunner, has revived the almost extinct hot-air balloon by means of a heating apparatus that can be carried aloft in the basket and continue to pour hot air into the bag in exactly regulated volumes, making for easy control of its lifting power and eliminating the need for ballast.

Herr Brunner's " bootstrap " invention consists of a simple type of burner which is easily prepared by any tinsmith. The fuel is crude oil. A pipe carries the burner up to the bottom opening of the balloon, and the spreading-ring there prevents the fabric from coming within igniting distance of the flame. Valves regulate the flame to any desired height. The cost for fuel per flight-hour is about $2.

C.

Atoms Like Magnetic Eggs.—(*Science Service.*) Dr. R. BECKER of Berlin has succeeded in showing that the atoms in a metal wire are rearranged under the influence of a magnetic field. In his experiment, a wire with a weight attached to its end was twisted, after which it oscillated for ten seconds before the vibrations ceased. A magnetic field, placed around the wire and parallel to it, so successfully lined up the atoms and overcame the internal friction, that the oscillations did not damp out for more than one hundred seconds.

In carrying Dr. Becker's work still further PROFESSOR FRANCIS BITTER of the Massachusetts Institute of Technology assumes that the tiny atoms of a metal are egg-shaped and free to turn so that if the metal is placed under tension the atoms will line up with their long axes pointing in the same direction as the applied force. By

magnetizing the metal before applying the force, Professor Bitter has found that a change in length of the metal is more easily obtained since the magnetization has already done the preparatory work of arranging the atoms with their long axes parallel. Conversely, if metal is stretched first, it will be much easier to magnetize, since stretching prepares the metal for further alterations, again by lining up the atoms.

C.

Giant Rubber Molecules.—(*Science Service.*) Anyone acquainted with no more than the elements of biology knows well the fundamental importance of the egg. What is more noteworthy is that within one week recently, public attention was directed to a physicist who assumes the atoms of metal to be egg-shaped and to a chemist who announces the discovery of egg-shaped molecules of rubber that can be seen with a microscope.

Although these egg-shaped units are giants among molecules they are just at the limits of the microscope. Their length is figured to be but six one-hundred-thousandths of an inch. Rubber molecules of these dimensions are believed to weigh 500,000 times as much as hydrogen atoms. Up to the present, synthetic rubber has been prepared on the basis that rubber molecules each weighed only 68,000 times as much as hydrogen. Professor George L. Clark made the discovery of the giant molecules when working in the x-ray laboratory of the University of Illinois. The reason for failure, Prof. Clark states, of science to see the actual molecules before was that they were embedded in a jelly-like substance which had not previously yielded to any breaking down process.

C.

Improved Paints Spur Attacks on Corrosion Problems.—J. O. HASSON. (*Steel*, Vol. 96, no. 10.) The annual toll of rust and corrosion of metals in service has been estimated to be $100,000,000 for the United States. Paint is a practical answer to the problem of rust prevention; but there are a hundred and one conditions to be met and a single type of paint cannot be expected to meet every situation to the best advantage.

Of the pigments in general use for corrosion inhibiting paints, red lead is one of the oldest and best known. Though satisfactory, as a primer, it tends to become too hard and brittle for a finishing coat, and is also fairly expensive. Litharge added up to about 10 per cent is claimed to increase the protective properties of red lead paint. Graphite paints containing sufficient pigment, though suitable for finishing coats are hardly desirable as primers.

From various tests on pigments reported by H. A. Gardner,

notably those made at Atlantic City, N. J., American Vermillion (basic lead chromate) easily ranks first. Sublimed blue lead ranks slightly lower.

Theoretically, no matter how valuable any pigment may be, it will fail utterly in metal protective value if the film cracks or becomes porous. The pigments and constituent elements of the oils and driers must be carefully balanced.

Finishing paints for applying over priming coats are even more varied in ingredients than most standard primers. Perhaps the steel finishing paint that has most to recommend it and is nearest to an all purpose metal protective paint is the combination graphite paint possessing the water shedding properties characteristic of carbon and graphite paints.

Among the factors that must be considered in deciding on a paint for unusual circumstances is its heat reflecting properties. The case of Piccard's balloon flights shows the effect of color. His first flight was in a black gondola. He nearly sweltered under a temperature of 100° F. The second flight in a white gondola made him suffer from a temperature below freezing. Yet the stratosphere temperature remains constant at −75° F. The Bureau of Mines Report 3138 shows the effect of paint color over a period of 4½ months on 12,000 gallon horizontal tanks.

Surfaces that are exposed to corrosive gases, acid or alkali fumes, weather of all kinds and underground conditions, require great care in not only selecting a coating but in applying one.

R. H. O.

Something New in Sail Boats.—(*Science Service.*) From Stockholm comes word that DR. FREDRIK LJUNGSTRÖM of the Academy of Engineering Sciences has invented a new type boat having a revolving mast on which the main sail is wound up like a window shade on its roller. The main sail is triangular but double. Running before the wind the double sail opens out into what looks like a great parachute jib sail. For tacking into the wind one sail lies smoothly on top of its mate.

Aerodynamic streamlining is achieved in the sail by having its forward edge fixed in a slot on the bow side of the forty-six foot pine mast. To reduce sail area, as in reefing, the navigator simply turns a wheel and rotates the mast by a system of ropes. Ball bearing rollers in the foot of the mast below deck makes this rotation easy.

The only stay on the boat is a tiny wire running from the tip of the mast to the stern of the boat. According to Dr. Ljungström, the lack of stays is one reason for the speed of the boat. Although the surface area of these wire stays may be small, they vibrate in

the wind and hence greatly increase their resistance to a breeze. This new type boat is surprisingly fast and has easily beaten larger boats against which it has sailed. It will come up quicker and sail nearer the wind than the usual type boat.

C.

A More Powerful Gasoline.—(*Science Service.*) By using a gasoline with ideal 100 octane antiknock rating, the Army has found a way to increase the power output of airplane engines by nearly a sixth to a third without increasing the weight of gasoline used. This new experimental aviation gasoline was composed half of iso-octane and half of good quality ordinary aviation gasoline with ethyl addition.

These superior gasolines will cost more per gallon than present aviation fuels but since they will contain more power per pound, they promise to be actually more economical.

C.

Looking Into a Diesel's Interior.—(*Science Service.*) Using special glass windows resisting temperatures up to 3,500 degrees Fahrenheit, aviation research scientists have just discovered how fuel oil burns in a Diesel engine. By photographing on a motion picture film at the rate of 2,500 frames per second, A. M. Rothrock of the National Advisory Committee for Aeronautics Laboratories was able to demonstrate beyond question just how the fuel burned in the cylinder of a Diesel engine.

Previously it had been supposed that the oil began to burn as soon as it came in from the fuel jets. However, Mr. Rothrock's film proves that combustion occurs only after the fuel fills the firing space. Now that it is possible to see or photograph what is going on inside the cylinder this new technique should speed research in the Diesel engine field. For example, heretofore the character of various types of fuel jets could be determined only roughly. Now with the new windows and high-speed photography rapid checks on performance can be obtained.

C.

Japan's Metal Industries Exhibition.—Word comes from Japan that a metal industries exhibition will take place in the Commercial Museum at Osaka. It will be of three weeks duration, opening on the tenth and closing on the thirty-first of May, 1935. All nations are invited.

An excellent idea of what Japanese workers are accomplishing in the field of metallographic research may be had from the series

of short abstracts of papers which recently have been published in *Kinzoku* (The Journal of Metals). Thus, H. NISHIMURA has investigated the microstructure of aluminum and its alloys and developed a new equilibrium diagram for the aluminum-copper system. T. KIKUTA has made a complete investigation of the growth of cast iron when heated at elevated temperatures.

H. IMAI has studied the heat treatment of bronze in relation to such phenomena as the expansion of cast bronze on annealing, effects of rates of cooling, and the cracking of beta bronze during quenching. I. OBINATA has investigated the beta transformations in the systems copper-zinc, copper-tin and copper-aluminum.

C. H. TONAMY, who is responsible for submitting these abstracts in English, records a number of interesting observations on the hardening of gun metal. He reports that when this alloy is held at 700° C. for two hours then quenched in water, it shows about 30 per cent. increase in strength and elongation compared with the original metal. A second paper describes the same author's work on the quenching of tin bronzes. Y. KUBOTA discusses practical methods for cementation. Very good results are had when graphite is painted over the surface of gears, then dried by heating. This will protect the surface against the formation of a soft spot because of decarburization during quenching.

C.

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